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INVESTIGATION OF SENSITIVITY OF COMPLEX REACTING SYSTEMS TO CHEMICAL REACTION RATES

John H. Schaibly, et al

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INVESTIGATION OF SENSITIVITY OF COMPLEX REACTING SYSTEMS TO CHEMICAL REACTION RATES

Annual Report

by

John H. Schaibly
Russell E. Duff

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13. ABSTRACT

Two methods have been developed to investigate the sensitivity of numerical solutions of sets of coupled non-linear differential equations to uncertainties in the modeling parameters entering the calculations. The methods determine the sensitivity by performing the calculations for a set of values of the modeling parameters within the estimated uncertainty range of each. The methods are demonstrated for two chemical reaction systems.

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1. INTRODUCTION

Systems, Science and Software (S^3) has begun a study to develop methods which can be used to determine the sensitivity of numerical solutions of sets of coupled differential equations to uncertainties in modeling parameters entering the calculations. The first year effort has been funded by the Advanced Research Projects Agency (ARPA) under ONR contract N00014-71-C-0347. This report describes work performed in this effort.

ARPA's interest in this problem has been stimulated primarily by a need on the part of the defense community to develop computational models to describe certain weapons effects in which non-equilibrium chemistry plays an important role. For such phenomena an accurate treatment of the kinetics of the chemical system requires that:

(1) All of the relevant species and the important reactions which occur among them are included.

(2) Accurate values of the important rate coefficients are known.

For many applications there is much debate, largely based on intuition, about which species are relevant, which reactions are important, and which rate coefficients must be known accurately. It is desirable, therefore, for ARPA to have at its disposal objective tools which can be used to help answer questions of priority for the allocation of their resources to experimental determinations of rate constants.

A second motivation for the research is to provide tools whereby the military and technical community can probe large complex systems to understand more fully the principles by which their constituent parts interact. In this respect, our methods are not limited to chemical systems, but may be applied to a wide variety of systems for which computational modeling is appropriate. For definiteness, however, the methods will be described in the context of non-equilibrium chemical systems to which they have been exclusively applied to date.

The methods which are being developed make use of the capability to solve the chemical kinetics problem several times for different values of the rate coefficients within their expected bands of uncertainty, and to interpret the results of these calculations in such a way as to determine the relative sensitivity of the results to the uncertainties in rate coefficients. It is useful to introduce the concept of an "output function" which in this report will mean a number which is of interest calculated from the model. Examples of output functions are:

- One of the concentrations at a particular time.
- A concentration maximum over all time.
- The time at which a concentration reaches some threshold.
- The maximum temperature attained by the system.
- The radiation intensity at a particular point in space at a specified time.

An output function is regarded as a function only of the rate coefficients of the model, and therefore uncertainties in the rate coefficients contribute to an uncertainty in the output function.

Since the dependence of an arbitrary output function will be, in general, a complicated, non-linear function of the rate coefficients, traditional analytical investigations are usually impossible. The importance of the various rate coefficients may not be determined by investigating each one separately holding the others fixed because of the complex interaction between reactions. Furthermore, the output function may be very sensitive to the rate coefficients in a localized region within the uncertainty limits rather than at the upper and lower bounds of uncertainty. Such regions would be missed by a sensitivity analysis which examined only maximum and minimum values of the rate coefficients.

Mathematically, the problem reduces to that of investigating a non-linear function of many variables over a domain of its arguments. The procedure is therefore characterized by two parts:

(1) Selection of a number of points at which one will evaluate the function.

(2) Determination of the relative sensitivity of the function to the various arguments on the basis of the function evaluations.

The methods which have been developed prescribe a sequence of values of rate coefficients at which the output function is evaluated. All of the rate coefficients vary simultaneously along the sequence of points. Two different approaches have been formulated which we shall call the Fourier method and optimization methods. In the Fourier method, the sequence of rate coefficient values for the analysis is prescribed before any calculations of the output function are obtained, whereas in the optimization methods, later points in the sequence are determined by the values of the output function calculated at earlier points. In the Fourier method only values of the output function are computed whereas some of the optimization methods require the calculation of various partial derivatives of the output function with respect to the various rate coefficients.

The methods are designed to accommodate output functions of an arbitrarily large number of rate coefficients, although the cost of performing the sensitivity analysis increases rapidly with this number. To date the methods have been applied only to the relatively simple systems described below. The systems are sufficiently simple that some results of the methods can be qualitatively verified by intuition or hindsight. The three systems which have been considered in some detail are:

(1) Various "simulation functions" which are merely analytical functions of several parameters.

(2) A chemical system describing the high temperature dissociation of air (five concentrations, ten reactions).

(3) A chemical system describing the combustion of hydrogen (six concentrations, eighteen reactions).

While these examples are extremely simple compared to the systems for which the methods are needed most, they do demonstrate the feasibility of the methods, and strongly suggest their applicability to more complex systems.

In order to apply the methods to chemical systems, one must be able to solve a set of chemical rate equations. Many techniques have been developed for such problems, and a code called KEM developed at S^3 using the Gear algorithm was used. Investigating the accuracy or efficiency of the integration technique or comparing various techniques was outside the scope of the research effort. The KEM calculation is essentially regarded as a subroutine which gives an output function for a specified set of rate coefficients.

In Sections 2.1 through 2.4 the formulation of the Fourier method is presented, and in Section 2.5 the results of the sensitivity analysis using this method for the two chemical systems described above is summarized. In Section 2.6 a Monte Carlo technique for obtaining the same results is compared to the Fourier method.

In Section 3.1 the optimization methods are described and in Section 3.2, comparisons of several optimization methods are described for a simulation function. In Section 3.3 an optimization method is applied to the air dissociation chemical system. In Section 4 a summary of the work and proposed extensions are presented.

2. THE FOURIER METHOD

2.1 FORMULATION OF THE METHOD

The Fourier method is an attempt to investigate certain characteristics of a scalar function of several variables over a convex domain by simply evaluating the function at a finite set of points within the domain. More specifically, the function is evaluated at a set of points along a curved line within the domain. While the formulation of the method is independent of the nature of the output function, and the variables on which it depends, the notation and phraseology of this discussion will reflect the context of a specific application in which the output function, f, is a concentration of a chemical species in an isothermal, constant density reacting system, and the independent variables k_i, $i = 1, n$ are the rate constants which appear in the kinetic equations which describe the reacting system. The region of interest in the k-space is that spanned by the estimated uncertainties in the current determination of the rate constants.

The curved line on which f is to be evaluated is defined by the single parameter, s, by the specification

$$k_i = k_i^o e^{u_i} \tag{2.1}$$

and

$$u_i = u_i^o \sin \omega_i s \ , \ i = 1, n \quad . \tag{2.2}$$

The introduction of the parameter s provides a convenient prescription for varying all of the rate constants simultaneously. By selecting a set of s values, a set of values of k are obtained distributed within the n dimensional uncertainty domain.

The modus operandi of the Fourier method is to select a set of distinct "input" frequencies $\{\omega_i\}$, one for each reaction rate being investigated. A set of values of s are also chosen, and the output function f is evaluated for each value (for the set of $\{k_i\}$ specified for each value of s through Equations (2.1) and (2.2)). f may thus be viewed as a function of s,

$$f(s) \equiv f[k_1(s), k_2(s), \ldots, k_n(s)] \quad , \tag{2.3}$$

and this function is Fourier analyzed to obtain the sine and cosine amplitudes corresponding to various frequencies.

2.2 QUALITATIVE INTERPRETATION OF THE FOURIER AMPLITUDES, INTERFERENCES, AND ALIASING

It is convenient to assume for the moment that all the frequencies are incommensurate (irrational). It is impossible to represent such frequencies in a digital computer, but the exercise sheds light on the qualitative interpretation of the amplitudes. Furthermore, it will be assumed that f is an analytic function of all the rate coefficients in the domain defined by the uncertainties. If the amplitudes corresponding to input frequency ω_i and its harmonics are very small, the uncertainty in the ith reaction rate is unimportant in determining the uncertainty of f. If, on the other hand, the amplitude of ω_i is large, the contribution from the uncertainty of the ith rate coefficient to the output function is large. In Section 2.4 the magnitude of the Fourier coefficient will be related to an average of $\partial f/\partial u$ over the u-space characterizing the uncertainties.

In practice, the unique identification of a frequency with the rate coefficient it represents may be obscured by two effects: interferences between frequencies, and aliasing. Interferences arise from the fact that incommensurate frequencies may not be chosen since they cannot be represented on a digital computer. Commensurate frequencies have the property that they cannot be linearly independent with respect to integer coefficients. If, for example,

$$\omega_1 + 2\omega_2 = \omega_3 \quad , \tag{2.4}$$

the amplitudes corresponding to ω_3 will reflect not only the effects of the uncertainty of k_3, but also k_1 and k_2 through the interference.

Aliasing arises whenever a finite number of points are chosen on the interval to evaluate the Fourier amplitude, and the effects are more serious when evenly spaced points are chosen. For example, if N equally spaced points are chosen,the amplitudes for ω_L will unavoidably include the amplitudes of a component with frequency ω_M present in f(s) which satisfies the relation

$$\omega_L = mN - \omega_M \tag{2.5}$$

where m is an arbitrary integer.

The current method takes the frequencies ω_i to be integers and evaluates the output function at evenly spaced discrete values of s on the interval $0 < s \leq 2\pi$. This choice was motivated by the goal of reducing as much as possible the number of points to be evaluated to obtain the Fourier amplitudes as shown in the next section.

2.3 CHOICE OF FREQUENCIES AND THE METHOD OF FOURIER ANALYSIS

The Fourier sine amplitude corresponding to an arbitrary frequency ω_L associated with the Lth rate coefficient is defined as

$$A_L = \lim_{T\to\infty} \frac{1}{T} \int_0^T \sin \omega_L s \; f[k_1(s), \ldots, k_n(s)]\, ds \quad , \tag{2.6}$$

and the cosine amplitude is defined as the same integral with the sine function replaced by a cosine function. Since this integral is to be performed numerically and it is important to minimize the number of s points used in the integral, it seems advantageous to replace this integral over the infinite interval by one over a finite interval. This may be done provided only rational frequencies are present in the function f. For output functions which are sufficiently smooth, one can insure that only rational frequencies appear by specifying that the input frequencies themselves are rational. It is convenient to further simplify the integral by the transformations in Appendix A which show that Equation (2.6) with rational frequencies reduces to Equation (2.7) with integer frequencies ω_i' defining the k's through Equations (2.1) and (2.2),

$$A_L = \frac{1}{2\pi} \int_0^{2\pi} ds \sin \omega_L' s \, f[k_1(s), \ldots, k_n(s)] \quad . \qquad (2.7)$$

In the remainder of this section, integer input frequencies will be assumed.

2.3.1 Choice of Noninterfering Frequencies

Since integer frequencies are to be input, various sums and differences of those frequencies will coincide. The frequencies must be chosen so as to minimize these interferences in some sense.

We define an interference of nth order as a linear combination of n frequencies with coefficients ±1. Thus, $\omega_1 - 2\omega_2$ is an interference of third order, while $\omega_1 - \omega_3 - 2\omega_2 - \omega_1$ is also an interference of third order, that is, $\omega_3 - 2\omega_2$.

In order to understand the meaning of the interference amplitudes in relation to the variation of the output function with the rate constants, it is convenient to consider f as a function of the various u_i instead of as a function of the k_i through the transformation in Equation (2.1). Assuming that f is a bounded, continuous function of u_i with partial derivatives of all orders in the region $-u_i^o \leq u_i \leq u_i^o$, it may be expanded in a Taylor series about the point $u_i = 0,\ i = 1,\ n$.

$$f(u_1, \ldots, u_n) = f_o + \sum_{i=1}^{n} \left(f_i u_i + f_{ii} u_i^2 + \ldots\right)$$

$$+ \sum_{i \neq j}^{n} \left(f_{ij} u_i u_j + f_{ijj} u_i u_j^2 + \ldots\right)$$

$$+ \sum_{i \neq j \neq k = 1}^{n} \left(f_{ijk} u_i u_j u_k + f_{iijk} u_i^2 u_j u_k\right.$$

$$\left. + f_{iiijk} u_i^3 u_j u_k + \ldots\right)$$

$$+ \ldots \tag{2.8}$$

where, for example,

$$f_{ij} = \frac{\partial^2 f}{\partial u_i \partial u_j} \frac{1}{2!} \quad . \tag{2.9}$$

The function f can also be expanded in a Fourier series

$$f(s) = B_o + \sum_{\ell=1}^{\infty} \left(A_\ell \sin \ell s + B_\ell \cos \ell s\right) . \tag{2.10}$$

Substituting $u_i = u_i^o \sin \omega_i s$ into Equation (2.8) a series is obtained, the terms of which contain products of various powers of trigonometric functions, i.e.,

$$\sin^p \omega_i s \sin^q \omega_j s \quad . \tag{2.11}$$

By using the identity

$$e^{i\omega_i sp} e^{i\omega_j sq} = e^{is(p\omega_i + q\omega_j)} \quad , \tag{2.12}$$

and realizing that $p\omega_i + q\omega_j$ is integer, one observes that the two series contain exactly the same terms making the identification of the A_ℓ, B_ℓ with various sums of partial derivatives evaluated at the point $u_i = 0$, $i = 1, n$. Furthermore, a p th order interference in the Fourier series arises from terms in the Taylor expansion of order p or greater. In fact, if f were linear in all u's, the only frequencies appearing the Fourier decomposition would be the input frequencies.

The assumption is tacitly made that, in general, high order interferences (and, therefore, high order terms in u) are small compared with lower order interferences and, therefore, it will be adequate to select the input frequencies in such a way as to eliminate effects of interferences below, say, Mth order. Interferences above Mth order will give rise to inaccuracies in the amplitudes. From the standpoint of interferences, therefore, one prefers to choose frequencies consistent with large M, which turn out to be relatively large integers. On the other hand, the number of output function evaluations necessary to evaluate the Fourier amplitudes of large frequencies is greater than that necessary for small frequencies. The method which has been investigated to date makes use of frequencies for which no interferences of the order of less than five coincide with the input frequencies.

2.3.1.1 Numerical Procedure for Determining the Frequencies

The method currently used to determine the integer input frequencies, ω_i, is essentially a trial and error procedure. The object is to find a set of n integers ω_i such that no interferences of the order of four or less will coincide with an input frequency. Explicitly,

$$p\omega_j + q\omega_k + r\omega_\ell + s\omega_m \neq \omega_i , \quad i \neq m \neq \ell \neq k \neq j$$

where $\omega_j, \omega_k, \omega_\ell, \omega_m$ and ω_i are input frequencies, and the coefficients obey

$$-4 \leq p, q, r, s \leq 4 \quad ,$$

and

$$|p| + |q| + |r| + |s| \leq 4 \quad . \tag{2.13}$$

An obvious simplification is made by chosing all odd integers for the input frequencies so that there are no coincidences with second order or fourth order interferences. The only conditions that remain to be satisfied are that

$$\omega_i - \omega_j \neq \omega_k - \omega_\ell \tag{2.14a}$$

and

$$\omega_i + \omega_j \neq \omega_k - \omega_\ell \quad . \tag{2.14b}$$

The first step is to find an ordered set of differences such that Equation (2.14a) is satisfied, that is, a set of d_i such that

$$d^*_m = \sum_{i=1}^{m} d_i \tag{2.15}$$

are distinct for $1 \leq m \leq n-1$. This is done recursively, and while there exist many solutions for a particular n, one wishes to find the set with the minimum largest difference d_{max}

$$d_{max} = \sum_{i=1}^{n-1} d_i \qquad (2.16)$$

which determines, in part, the largest frequency.

The process proceeds as follows. A table is begun for $n=3$, with the ordered set of frequencies $\omega_1 < \omega_2 < \omega_3$, and the ordered set of differences, $d_1 = \omega_2 - \omega_1$, and $d_2 = \omega_3 - \omega_2$. d_i are determined to be the smallest possible even numbers (excepting 2), i.e.,

$$d_1 = 4 \quad , \quad d_2 = 6 \quad .$$

The difference $d_2^* = d_1 + d_2 = 10$ also occurs and is distinct from d_1 and d_2. It is convenient to express the results in a triangular table

```
4   6
10      .
```

To continue the process for $n=4$, one chooses $d_3 = 8$ (must be distinct) and the d^* are determined by forming the diagonal as shown below

i =	1	2	3
	4	6	8
	10	14	
	18		

from upper right to lower left $(i=n-1,\ i=1)$, the element in the i th column being the sum of the diagonal in the $i+1$ st column and the difference appearing at the top of the i th column. The successive d_i are chosen so that no number in the entire table is repeated.

One is not restricted to choosing the next d_i to be the lowest unused even integer, but experience shows that as a general rule this choice will result in the lower frequencies. Two sets of differences have been calculated and are presented in Tables 2.1 and 2.2. The set of differences in Table 2.1 use the lowest possible unused difference to increment n, while in Table 2.2 d_2 was taken not to be the lowest unused even number, 6, but 8. It appears that the frequencies from either method are equally good, and that the results are not strongly dependent on the ordering of small differences. Furthermore, since the even numbers between d_1 and d_n which are omitted is relatively small, it appears that little improvement could be made by finding the optional ordering since d_{max} would not change significantly.

The set of differences for n ordered frequencies is the set of the first $n - 1$ differences of the top row in either table. For example, for $n = 6$, the differences in Table 2.2 are: 4, 8, 6, 10, 20.

After a set of differences are found for a particular n, the whole set of frequencies is determined by specifying the lowest frequency. In the example above, with $n=6$, one assigns the differences in reverse order and assigns $\omega_1 = 1$ to obtain the frequency set: 1, 21, 31, 37, 45, 49. The second step is to add to all frequencies the same integer until Equation (2.14b) is satisfied,

$$\omega_i + \omega_j \neq \omega_k - \omega_\ell \quad . \tag{2.17}$$

Frequencies for which no interferences of order less than 5 coincide with an input frequency have been calculated for $n \leq 19$ and the frequency sets are shown in Table 2.3.

Table 2.1

SET OF DIFFERENCES FOR WHICH $d^*_m = \sum_{i=1}^{m} d_i$ ARE DISTINCT, $d_2 = 6$

4	6	8	12	16	22	32	24	48	40	34	76	60	98	62	66	52	152	188	86	132	108	176	84	148
10	14	20	28	38	54	56	72	88	74	110	136	158	160	128	118	204	340	274	218	240	284	260	232	
18	26	36	50	70	78	104	112	122	150	170	234	220	226	180	270	392	426	406	326	416	368	408		
30	42	58	82	94	126	144	146	198	210	268	296	286	278	332	458	478	558	514	502	500	516			
46	64	90	106	142	166	178	222	258	308	330	362	338	430	520	544	610	666	690	586	648				
68	96	114	154	182	200	254	282	356	370	396	414	490	618	606	676	718	842	774	734					
100	120	162	194	216	276	314	380	418	436	448	566	678	704	738	784	894	926	922						
124	168	202	228	292	336	412	442	484	488	600	754	764	836	846	960	978	1074							
172	208	236	304	352	434	474	508	536	640	788	840	896	944	1022	1044	1126								
212	242	312	364	450	496	540	560	688	828	874	972	1004	1120	1106	1192									
246	318	372	462	512	562	592	712	876	914	1006	1080	1180	1204	1254										
322	378	470	524	578	614	744	900	962	1046	1114	1256	1264	1352											
382	476	532	590	630	766	932	986	1094	1154	1290	1340	1412												
480	538	598	642	782	954	1018	1118	1202	1330	1374	1488													
542	604	650	794	970	1040	1150	1226	1378	1414	1522														
608	656	802	982	1056	1172	1258	1402	1462	1562															
660	808	990	1068	1188	1280	1434	1486	1610																
812	996	1076	1200	1296	1456	1518	1634																	
1000	1082	1208	1308	1472	1540	1666																		
1086	1214	1316	1484	1556	1688																			
1218	1322	1492	1568	1704																				
1326	1498	1576	1716																					
1502	1582	1724																						
1586	1730																							
1734																								

Table 2.2

SET OF DIFFERENCES FOR WHICH $d_m^* = \sum_{i=1}^{m} d_i$

ARE DISTINCT, $d_2 = 8$

4	8	6	10	20	22	32	40	38	26	56	62	46	76	96	60	86	126	134	112	92	128	154	196	34
12	14	16	30	42	54	72	78	64	82	118	108	122	172	156	146	212	260	246	204	220	282	350	230	
18	24	36	52	74	94	110	134	120	144	164	184	218	232	242	272	346	372	338	332	374	478	384		
28	44	58	84	114	132	136	160	182	190	240	280	278	318	368	406	458	464	466	486	570	512			
48	66	90	124	152	158	192	222	226	266	336	340	364	444	502	518	550	592	620	682	604				
70	98	130	162	178	214	254	268	304	362	396	426	490	578	614	610	678	746	816	716					
102	138	168	188	234	276	300	344	400	422	482	552	624	690	706	738	832	942	850						
142	176	194	244	296	322	376	440	460	506	608	686	736	782	834	892	1028	976							
180	202	250	306	342	398	472	500	546	634	742	798	828	910	968	1088	1062								
206	258	312	352	418	494	532	586	672	768	854	890	956	1064	1184	1122									
262	320	358	428	514	554	618	712	806	880	946	1018	1110	1260	1218										
324	366	434	524	574	640	744	846	918	972	1074	1172	1306	1294											
370	442	530	584	660	766	878	958	1010	1100	1228	1368	1340												
446	538	590	670	786	900	990	1050	1138	1254	1424	1402													
542	598	676	796	920	1012	1082	1178	1292	1450	1458														
602	684	802	930	1032	1104	1210	1332	1488	1484															
688	810	936	1042	1124	1232	1364	1528	1522																
814	944	1048	1134	1252	1386	1560	1562																	
948	1056	1140	1262	1406	1582	1594																		
1060	1148	1268	1416	1602	1616																			
1152	1276	1422	1612	1636																				
1280	1430	1618	1646																					
1434	1626	1652																						
1630	1660																							
1664																								

Table 2.3

FREQUENCY SETS AND CORRESPONDING NUMBER OF POINTS AVOIDING INTERFERENCES AND ALIASES OF INTERFERENCES THROUGH 4th ORDER

Dimensionality	Frequency Set	Minimum Number of Points
5	11, 21, 27, 35, 39	142
5*	2, 42, 62, 74, 90	191
6	1, 21, 31, 37, 45, 49	182
6*	2, 42, 62, 74, 90, 98	231
7	17, 39, 59, 69, 75, 83, 87	334
8	23, 55, 77, 97, 107, 113, 121, 125	486
9	19, 59, 91, 113, 133, 143 149, 157, 161	630
10	25, 63, 103, 135, 157, 177, 187, 193, 201, 205	806
11	41, 67, 105, 145, 177, 199, 219, 229, 235, 243, 247	974
12	31, 87, 113, 151, 191, 223, 245, 265, 275, 281, 289, 293	1158
13	23, 85, 141, 167, 205, 245, 277, 299, 319, 329, 335, 343, 347	1374
14	87, 133, 195, 251, 277, 315, 355, 387, 409, 429, 439, 445, 453, 457.	1814
15	67, 143, 189, 251, 307, 333, 371, 411, 443, 465, 485, 495, 501, 509, 513	2038
16	73, 169, 245, 291, 353, 409, 435, 473, 513, 545, 567, 587, 597, 603, 611, 615	2446
17	85, 145, 241, 317, 363, 425, 481, 507, 545, 585, 617, 639, 659, 669, 675, 683, 687	2734
18	143, 229, 289, 385, 461, 507, 569, 625, 651, 689, 729, 761, 783, 803, 813, 819, 827, 831	3310
19	149, 275, 361, 421, 517, 593, 639, 701, 757, 783, 821, 861, 893, 915, 935, 945, 951, 959, 963	3848

*These sets of 5 and 6 frequencies are not minimal, but have been used and are only included for completeness. They are also free of inteferences and aliases of order less than 5.

2.3.2 Fourier Analysis and Avoidance of Aliases

The Fourier analysis could be performed either by evaluating f at N evenly spaced or unevenly spaced points on the interval $(0, 2\pi)$. Evenly spaced points are chosen although it is not certain that it is an optional choice. Given evenly spaced points, however, it is convenient to replace the integral in Equation (2.7) by a sum. Consider the sum

$$A^*_L = \frac{2}{N} \sum_{\ell=1}^{N} \sin\left(\omega_L \frac{2\pi\ell}{N}\right) f\left(\frac{2\pi\ell}{N}\right) . \tag{2.18}$$

It is shown in Appendix B that

$$A^*_L = A_L + \text{error} \quad , \tag{2.19}$$

where the error terms called "alias amplitudes" are the amplitudes of various interference frequencies:

$$\text{error} = \sum_{m=0}^{\infty} \sum_{j} A_{(mN - \omega_j)} \quad , \tag{2.20}$$

where ω_j is any frequency appearing in f satisfying the relation

$$mN - \omega_j = \omega_L , \tag{2.21}$$

where m is an arbitrary integer. The number N is chosen so that Equation (2.21) is not satisfied for ω_j an interference of order less than 5 and ω_L is any input frequency. This number is determined by calculating for a trial $\overline{N}$

$$m\overline{N} - \omega_L$$

where ω_L is an input frequency, and comparing this number with each interference frequency through fourth order. N is the minimum value of $\overline{N}$ for which there are no coincidences. The number N for the frequency sets in Table 2.3 is also shown.

2.4 QUANTITATIVE INTERPRETATION OF THE FOURIER AMPLITUDES; ALTERNATE WEIGHT FUNCTIONS IN u SPACE

One can view the Fourier method as being characterized by a sampling prescription in n-dimensional u space in addition to an analysis of the output function evaluated at the selected points. The result of the method depends of all the points sampled, and we show below that certain Fourier amplitudes are related to averages of the output function with various weight functions over the n-dimensional u space.

It is shown in Appendix C that if f is a polynomial function of the u's of order p-1, and the input integer frequency set is chosen so that no interferences of order less than p coincide with input frequencies, then the one-dimensional integral corresponding to the sine amplitude of input frequency ω_L is equal to an n-dimensional integral over u space:

$$A_L \equiv \frac{1}{2\pi} \int_0^{2\pi} ds\; f(u_1(s),\, u_2(s) \ldots u_n(s)) \sin\; \omega_L s$$

$$= \frac{1}{\pi^n} \int_{-u_1^o}^{u_1^o} du_1 \int_{-u_2^o}^{u_2^o} du_2 \ldots \int_{-u_n^o}^{u_n^o} du_n \; \frac{u_L}{u_L^o} \; \frac{f(u_1,\, u_2,\, \ldots u_n)}{\prod_{i=1}^{n} u_i^o \sqrt{1-\left(\frac{u_i}{u_L^o}\right)^2}} \;. \qquad (2.22)$$

(This equality does not hold for functions f of order higher than p-1 and an error term appears proportional to $(f^{(p)}/2^{p-1})$ as shown in Appendix C.) This

Fourier amplitude is therefore equal to the Lth component of the centroid, weighted by the function

$$W(\bar{u}) = \frac{1}{\prod_{i=1}^{n} \sqrt{1 - \left(\frac{u_i}{u_i^o}\right)^2}} \quad . \tag{2.23}$$

An alternative form of the multiple integral may be derived by integrating by parts with respect to u_L, i.e.,

$$A_L = \frac{1}{\pi^n} \int_{-u_1^o}^{u_1^o} du_1 \ldots \int_{-u_n^o}^{u_n^o} du_n \, u_L^o \sqrt{1 - \left(\frac{u_L}{u_L^o}\right)^2} \, \frac{\partial f}{\partial u_L} \, \frac{1}{\prod_{i=1}^{n} \sqrt{1 - \left(\frac{u_i}{u_i^o}\right)^2} \, u_i^o} \tag{2.24}$$

The weight functions in these multiple integrals emphasize various regions of u-space. In the form in Equation (2.22), all edges of the hypercube are emphasized equally, whereas in the integral in Equation (2.24), the distribution is uniform in u_L but emphasizes the edges in the other dimensions. Efforts to modify this weighting will be described below.

The implication of Equation (2.24) is that the Fourier coefficient may be interpreted as an average over the whole uncertainty region of $\partial f/\partial u_L$, and it therefore represents a measure of sensitivity. Alternatively, by analyzing ℓnf instead of f one obtains the measure of sensitivity of the relative uncertainty in f to the uncertainty of the various rate coefficients, i.e., an average of $\frac{1}{f}\frac{\partial f}{\partial u_L}$.

The estimated experimental uncertainty, u_i^o, represents the half width of some distribution of probable values for the reaction rate. Therefore, one can argue that the sampling procedure should emphasize the region of u-space near the origin. The appearance of the weight functions which emphasize the boundaries of the region may therefore be undesirable. One can alter the weight function by choosing an alternative definition of u_i (see Equation (2.2):

$$u_i = u_i^o v_i (\sin \omega_i s_i) \quad , \tag{2.25}$$

and choosing v_i to be a monotonic function of $\sin \omega_i s$.

We will demonstrate this by finding v_i such that the weighting function in Equation (2.22) is given by

$$W(\bar{u}) = \prod_{i=1}^{n} e^{-u_i^2/u_i^{o2}} \quad . \tag{2.26}$$

Assuming that f is a polynomial in the u's of order $p-1$, and using the same argument as those in Appendix C, one can show that

$$A_L \equiv \frac{1}{(2\pi)} \int_0^{2\pi} ds \sin \omega_L s \, f(u_1(s), \ldots, u_n(s))$$

$$= \frac{1}{\pi^n} \int_{-u_1^o}^{u_1^o} du_1 \cdots \int_{-u_n^o}^{u_n^o} du_n \frac{u_L}{u_L^o} \prod_{i=1}^{n} \frac{ds_i}{du_i} \omega_i f(u_1, u_2, \ldots u_n) \quad . \tag{2.27}$$

Setting

$$\frac{ds_i}{du_i} = \frac{1}{u_i^o} \frac{ds_i}{dv_i} \propto \frac{1}{\omega_i} e^{-u_i^2/u_i^{o2}} \tag{2.28}$$

one may solve for $v_i(s_i)$. A solution for this equation for $-1 \leq v_i \leq 1$ is

$$v_i(b_i) = \mathrm{erf}^{-1}\left(\frac{2\,\mathrm{erf}(1)}{\pi}\sin^{-1} b_i\right), \quad b_i > 0, \quad v_i(-b_i) = -v_i(b_i) \tag{2.29}$$

where

$$b_i = \sin \omega_i s_i \tag{2.30}$$

and

$$-\pi/2 \leq \sin^{-1} b_i \leq \pi/2 \quad .$$

This gives for the right side of Equation (2.27)

$$\frac{1}{(2\mathrm{erf}(1))^n} \int_{-u_1^o}^{u_1^o} du_1 \cdots \int_{-u_n^o}^{u_n^o} du_n \, \frac{u_L}{u_L^o} \prod_{i=1}^{n} e^{-\left(\frac{u_i}{u_i^o}\right)^2} \frac{1}{u_i^o} \, f(u_1, u_2, \ldots, u_n) \, . \tag{2.31}$$

One can integrate this by parts over u_L to obtain an average of $\partial f/\partial u_L$ with a Gaussian weight function remaining over all u's except u_L, and a weight function in the u_L dimension proportional to

$$H(u_L) = \int_{-\infty}^{u_L^o} du'_L \, u'_L e^{-(u'_L/u_L^o)^2} - \int_{-\infty}^{u_L} du'_L \, u'_L \, e^{-(u'_L/u_L^o)^2} \tag{2.32}$$

which is also peaked near $u_L = 0$.

Some calculations reported in the next section used this formulation of the Fourier method, but the results do not differ significantly from those obtained with the original formulation.

2.5 APPLICATIONS OF THE FOURIER METHOD

The Fourier method has been applied to various simulation functions (analytical functions) and to results calculated from models of two chemical systems. The results for the chemical systems will be presented in this section.

2.5.1 The Nitrogen-Oxygen (N-O) System

The N-O system is modeled by the following set of chemical reactions, rate constants and equilibrium constants:

$$O_2 + M \rightleftarrows 2O + M \qquad k_1, K_1$$

$$N_2 + M \rightleftarrows 2N + M \qquad k_2, K_2$$

$$NO + M \rightleftarrows N + O + M \qquad k_3, K_3$$

$$N_2 + O \rightleftarrows NO + N \qquad k_4, K_4$$

$$O_2 + N \rightleftarrows NO + O \qquad k_5, K_5$$

and is characterized by the following rate equations,

$$\frac{dc_1}{dt} = -k_1\left(c_1 M - \frac{1}{K_1} c_2^2 M\right) - k_5\left(c_1 c_4 - \frac{1}{K_5} c_5 c_2\right) ,$$

$$\frac{dc_2}{dt} = 2k_1\left(c_1 M - \frac{1}{K_1} c_2^2 M\right) + k_5\left(c_1 c_4 - \frac{1}{K_5} c_5 c_2\right) + k_3\left(c_5 M - \frac{1}{K_3} c_2 c_4 M\right) - k_4\left(c_3 c_2 - \frac{1}{K_4} c_5 c_4\right),$$

$$\frac{dc_3}{dt} = -k_2\left(c_3 M - \frac{1}{K_2} c_4^2 M\right) - k_4\left(c_3 c_2 - \frac{1}{K_4} c_5 c_4\right),$$

$$\frac{dc_4}{dt} = 2k_2\left(c_3 M - \frac{1}{K_2} c_4^2 M\right) + k_3\left(c_5 M - \frac{1}{K_3} c_2 c_4 M\right)$$

$$+ k_4\left(c_3 c_2 - \frac{K_5}{K_4} c_4\right) - k_5\left(c_1 c_4 - \frac{1}{K_5} c_5 c_2\right) ,$$

and

$$\frac{dc_5}{dt} = -k_3\left(c_5 M - \frac{1}{K_3} c_4 c_2 M\right) + k_4\left(c_3 c_2 - \frac{1}{K_4} c_5 c_4\right)$$

$$+ k_5\left(c_1 c_4 - \frac{1}{K_5} c_5 c_2\right) \qquad (2.33)$$

where

$c_1 = [O_2]$

$c_2 = [O]$

$c_3 = [N_2]$

$c_4 = [N]$

$c_5 = [NO]$

and

$$M = \sum_{i=1}^{5} c_i \quad . \qquad (2.34)$$

The assumption of equal reaction rates with each species acting as a third body, M, for reactions 1, 2, and 3 simplifies the system. k_i are the rate constants for the reaction in the forward direction as written, and K_i are the equilibrium constants. The rate constants for the reverse reactions are related to k_i by the relation

$$K_i = \frac{k_i}{k_{i\ \mathrm{reverse}}} \quad . \tag{2.35}$$

The system was assumed to react at constant temperature, 6000°K, and constant density beginning at $t = 0$ with only N_2 and O_2 present. The reaction rates and equilibrium constants used and the initial conditions assumed are shown in Table 2.4. A plot of the time evolution of this system is shown in Figure 2.1.

This chemical system is interesting because it has in addition to the monotonic concentrations, the NO concentration which passes through a maximum near $t = 10^{-4}$ sec.

The rate constants in Table 2.4 represent experimentally obtained rate coefficients, and while the uncertainties of these particular rate constants are not large, it was arbitrarily assumed that the experimental uncertainties for all the coefficients was ±2 orders of magnitude. In the sensitivity analysis, values of the rate coefficients were investigated lying in the range

$$k_i = k_i^o \, e^{\pm 4.606} \quad , \qquad i = 1, 5 \quad . \tag{2.36}$$

Throughout the course of the study, various sets of frequencies were used, some were not the minimal set described earlier, but all sets had the property that no interferences of the order less than 5 coincide with a fundamental. The most common set of frequencies used was

(2, 42, 62, 74, 90)

for which the lowest number of evenly spaced points which avoids aliasing of fourth order interferences is 191.

Table 2.4

PARAMETERS AND INITIAL CONDITIONS FOR CALCULATIONS OF THE N-O SYSTEM

Initial Conditions

$[N_2] = 8 \times 10^{-8}$ moles/cc

$[O_2] = 2 \times 10^{-8}$ "

Nominal Values of the Rate Coefficients

$k_1^o = 8.5 \times 10^{10}$ (moles/cc)$^{-1}$ sec^{-1}

$k_2^o = 3.0 \times 10^{7}$ "

$k_3^o = 8.0 \times 10^{9}$ "

$k_4^o = 9.0 \times 10^{10}$ "

$k_5^o = 8.0 \times 10^{11}$ "

Equilibrium Constants

$K_1 = 7.8 \times 10^{-4}$ (moles/cc)

$K_2 = 1.0 \times 10^{-7}$ "

$K_3 = 1.3 \times 10^{-5}$ "

$K_4 = 9.0 \times 10^{-3}$ -

$K_5 = 5.9 \times 10^{1}$ -

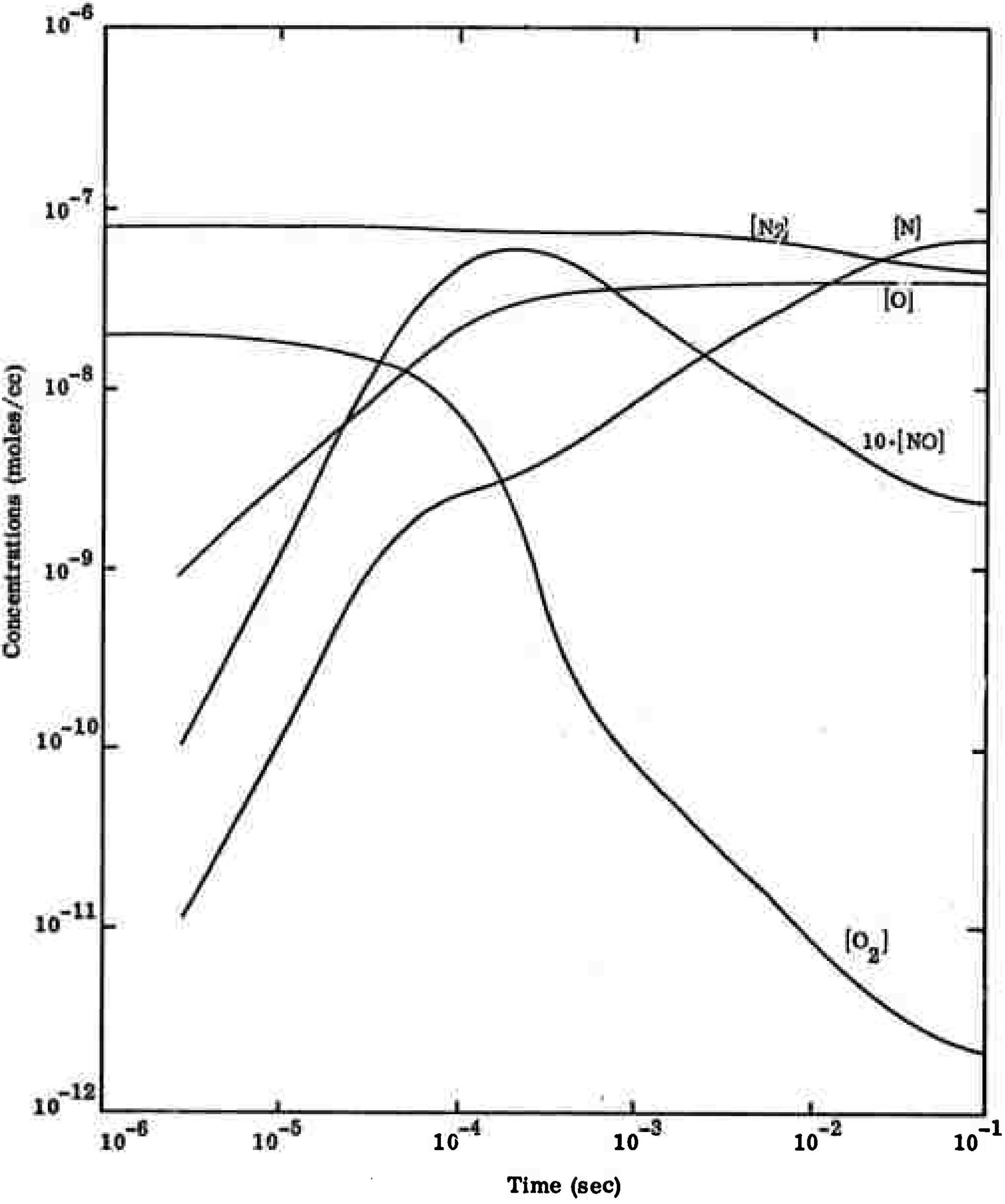

Figure 2.1 — Time evolution of the N-O system for the conditions in Table 2.4.

Parameterizing the rate constant parameters, u by the relation

$$u_i = 4.606 \sin \omega_i s \tag{2.37}$$

and varying s in the range $0 \leq s \leq 2\pi$, the concentrations of the various species were calculated by integrating the rate Equations (2.2) to a particular time for each of the 191 s values. The 191 values of a concentration at a particular time defines an output function which may be Fourier analyzed by computing the Fourier coefficients corresponding to the input frequencies according to formula

$$A_L = \frac{2}{N} \sum_{\ell=1}^{N} \sin \frac{2\pi \ell L}{N} \, f\left(\frac{2\pi\ell}{N}\right) , \quad N = 191 \tag{2.38}$$

where $f\left(\frac{2\pi\ell}{N}\right)$ is the output function evaluated at $s = \frac{2\pi\ell}{N}$. The relative magnitudes of these amplitudes is taken to be a measure of the relative sensitivity of the uncertainty in the output function to uncertainty in the corresponding rate coefficients.

As an example of f(s), Figure 2.2 shows a plot of the NO concentration as a function of s at $t = 10^{-4}$ sec. The curve consists of points corresponding to the NO concentration for each discrete value of s, which have been connected by straight lines. The Fourier coefficients of this function are presented in Section 2.5.1.2.

2.5.1.1 Interpretation of Results for the N-O System at 10^{-6} sec

The N-O system was run to a time of 10^{-6} sec and the Fourier analysis done on the concentrations at that time. The results for this calculation are presented in Table 2.5.

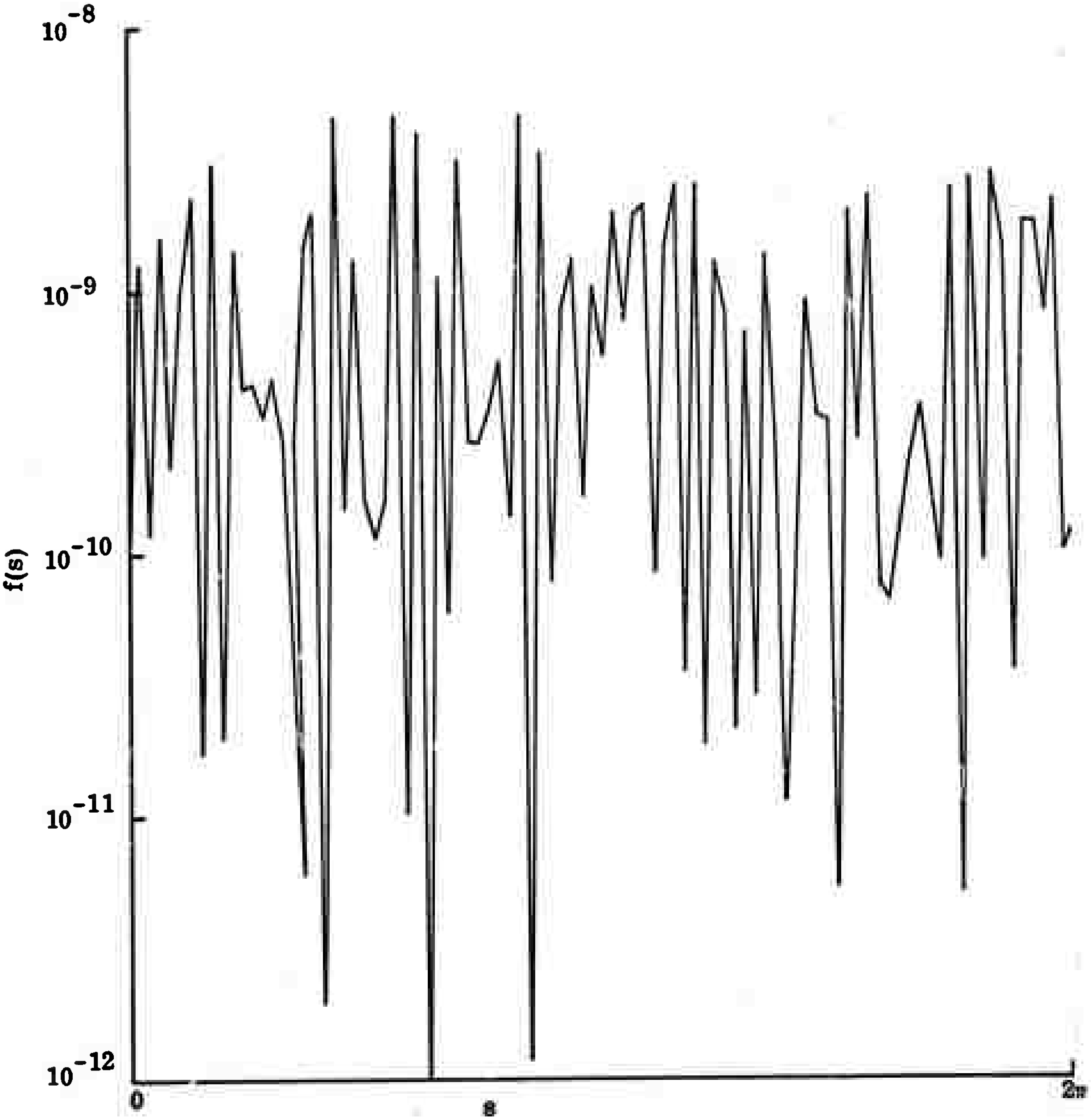

Figure 2.2 – Example of an output function as a function of s. In this case the output function is defined to be the concentration of NO at t = 10(-4) sec for the particular set of initial conditions in Table 2.4.

Table 2.5

SENSITIVITY OF THE CONCENTRATIONS AT 10^{-6} SEC TO UNCERTAINTIES IN THE RATE COEFFICIENTS FOR THE N-O SYSTEM

Input Frequency	Corresponding Rate Coefficient	Sensitivity
	$[O_2] \times 10^9$	
2	k_1	-4.47
90	k_5	-0.0244
74	k_4	-0.0227
42	k_2	-0.00047
62	k_3	-0.00039
	$[O] \times 10^9$	
2	k_1	8.53
74	k_4	-0.36
90	k_5	0.018
62	k_3	-0.029
42	k_2	0.0027
	$[N_2] \times 10^9$	
2	k_1	-0.389
74	k_4	-0.386
42	k_2	-0.0087
62	k_3	-0.0039
90	k_5	-0.00103
	$[N] \times 10^9$	
2	k_1	0.367
74	k_4	0.362
90	k_5	-0.028
62	k_3	-0.013
42	k_2	-0.011
	$[NO] \times 10^{10}$	
2	k_1	0.412
74	k_4	0.410
90	k_5	0.031
42	k_2	-0.0066
62	k_3	-0.0048

In the column labeled "Sensitivity" are listed the Fourier amplitudes corresponding to the rate coefficient shown. At this early time (see Figure 2.1) only reaction 1 is important in the production of O from O_2 and, thus, only the uncertainty in k_1 contributes to these concentrations. The sign of the amplitude may be understood by Equation (2.24) showing the amplitude proportional to an average of $\partial f/\partial u$. Thus, the negative sign in the sensitivity of O_2 to k_1 means that $\partial f/\partial k_1$ is negative, as one would expect. Since k_2 is small, the primary source of N is through reaction 4. One can show that at these early times, when the O_2 and N_2 are not substantially depleted, the concentrations of NO and N will be proportional to the product k_1k_4. The Fourier coefficients of these species are therefore (approximately) symmetric in k_1, k_4.

It is desirable that the results are independent of the input frequencies. Small amplitudes can depend strongly on the input frequency set through interferences obscuring the fundamentals. This provides a means for estimating the effects of interferences and aliases; for example, one can reassign the frequencies to the various rate constants and repeat the analysis. If the relative sensitivity is invariant under permutations, the result is reliable. If it varies with permutation, the result is questionable. For the amplitudes in Table 2.5 only the smallest amplitudes will be unreliable. A comparison of results under permutation is presented below for another set of output functions.

2.5.1.2 Interpretation of Results for the N-O System at 10^{-4} sec

The N-O system with the same initial conditions and rate constant specification was run to $t = 10^{-4}$ sec, and the various concentrations were analyzed with the results shown in Table 2.6.

Since the time is later, more reactions (and more uncertainties) have come into play. If we arbitrarily choose a factor of 10 to separate the "important" from the "unimportant" rate uncertainties, $[O_2]$ and $[O]$ are sensitive only to

Table 2.6

SENSITIVITY OF THE CONCENTRATION AT 10^{-4} SEC TO UNCERTAINTIES IN THE RATE COEFFICIENTS FOR THE N-O SYSTEM

Input Frequency	Corresponding Rate Coefficient	Sensitivity
	$[O_2] \times 10^8$	
2	k_1	-1.1
90	k_5	-0.147
74	k_4	-0.087
62	k_3	-0.069
42	k_2	-0.044
	$[O] \times 10^8$	
2	k_1	2.17
62	k_3	0.228
90	k_5	0.164
42	k_2	0.078
74	k_4	-0.00146
	$[N_2] \times 10^9$	
74	k_4	-2.6
2	k_1	-2.3
62	k_3	-1.0
90	k_5	-0.70
42	k_2	-0.55
	$[N] \times 10^9$	
2	k_1	4.3
74	k_4	3.3
62	k_3	3.0
42	k_2	0.98
90	k_5	0.125
	$[NO] \times 10^9$	
74	k_4	1.77
90	k_5	1.29
62	k_3	-0.91
2	k_1	0.23
42	k_2	0.124

the uncertainty in k_1. On the other hand, the other concentrations depend on several uncertainties. It is interesting that the most direct route to produce N, reaction 2, is relatively unimportant in determining any concentration.

In order to investigate possible errors in these results due to frequency interference effects, an additional analysis was made changing the frequencies assigned to the various rate coefficients. A cyclic permutation of the frequencies was used which caused different interferences of order ≥ 5 to coincide with the fundamentals. The problem for which this comparison was made was the same as that described in Table 2.4 except that one equilibrium constant, K_5, was changed to 5.9×10^{-1} which changed the reverse reaction rate, k_5. The results of this calculation are presented in column II of Table 2.7. The problem with modified K_5 was also run using the same frequency set as that used in Table 2.6 and the results presented in the column labled "I" so that direct comparison is possible. Only the small amplitudes are changed significantly. In no case did the sign change due to permutation although the rank based on the magnitude of the various small amplitudes changes occasionally.

In Section 2.4 an alternative parameterization of k_1 in terms of the parameters was discussed which resulted in a Gaussian weight function for the multi-dimensional integral. In columns III and IV the results for the same N-O system with modified K_5 are presented, with the original frequency set used in column III and the permuted set used in column IV. Again, significant differences due to permutation occur only in the relatively small coefficients. It is interesting to compare the results in columns I and III due to the different sampling of points. The formulation in column I favors points near the extremes of the uncertainty ranges. The general tendency for the magnitude of the amplitudes to be slightly smaller in column III indicates that $\partial f/\partial u$ tends to increase with u in general. There do not seem to be significant differences in the results between parameterizations of k_1. Moreover, the more complex parameterization will, in

Table 2.7

EFFECTS OF PERMUTATION OF FREQUENCIES AND ALTERNATE WEIGHT FUNCTIONS ON SENSITIVITY ANALYSIS, CONCENTRATIONS AT 10^{-4} SEC FOR THE N-O SYSTEM

Rate Coefficient	I	II	III	IV
$[O_2] \times 10^8$				
k_1	-1.14	-1.14	-1.05	-1.04
k_5	-0.040	-0.038	-0.0098	-0.036
k_3	-0.046	-0.045	-0.0248	-0.047
k_2	-0.028	-0.038	-0.0097	-0.016
k_4	-0.018	-0.020	-0.0030	-0.030
$[O] \times 10^8$				
k_1	2.27	2.28	2.08	2.05
k_3	0.124	0.127	0.074	0.111
k_5	0.105	0.097	0.031	0.075
k_2	0.045	0.069	0.015	0.034
k_4	-0.041	-0.039	-0.074	-0.152
$[N_2] \times 10^8$				
k_1	-0.569	-0.555	-0.428	-0.303
k_4	-0.465	-0.456	-0.292	-0.246
k_5	-0.290	-0.309	-0.159	-0.146
k_3	-0.069	-0.066	-0.035	-0.058
k_2	-0.045	-0.078	-0.023	-0.022
$[N] \times 10^8$				
k_1	1.12	1.09	0.836	0.693
k_4	0.853	0.838	0.504	0.400
k_5	0.597	0.640	0.360	0.331
k_3	0.171	0.169	0.093	0.137
k_2	0.079	0.149	0.012	0.046
$[NO] \times 10^{10}$				
k_4	7.71	7.76	7.99	9.28
k_3	-3.31	-3.70	2.40	2.37
k_5	-1.71	-2.17	4.07	3.96
k_1	1.40	1.58	2.06	3.33
k_2	1.06	0.721	0.395	0.316

I Sensitivity with frequency set (2, 42, 62, 74, 90) corresponding to $(k_1, \dots, k_5)$.

II Sensitivity with permuted frequencies (62, 74, 90, 2, 42) corresponding to $(k_1, \dots, k_5)$.

III Sensitivity using alternate form, Equations (2.25, and 2.29) with frequency set (2, 42, 62, 74, 90).

IV Sensitivity using alternate form, Equations (2.25 and 2.29) with frequency set (62, 74, 90, 2, 42).

general, increase the interferences (although it did not seem to for the N-O system). We, therefore, tend to favor the simple prescription.

The results of the sensitivity analysis for this simple N-O system agree with intuition in the cases where intuition gives an answer. Furthermore, ambiguity in the results due to frequency interferences is small for determining large sensitivity *vs* small sensitivity, but the small sensitivities may be quantitatively ambiguous.

2.5.2 The Hydrogen-Oxygen System

The H-O system is modeled by the following set of chemical reactions:

$H_2 + M \rightleftarrows 2\,H + M$	k_1, K_1
$O_2 + M \rightleftarrows 2\,O + M$	k_2, K_2
$OH + M \rightleftarrows O + H + M$	k_3, K_3
$H_2O + M \rightleftarrows H + OH + M$	k_4, K_4
$H + O_2 \rightleftarrows OH + O$	k_5, K_5
$O + H_2 \rightleftarrows OH + H$	k_6, K_6
$H_2 + OH \rightleftarrows H_2O + H$	k_7, K_7
$O_2 + H_2 \rightleftarrows 2\,OH$	k_8, K_8
$OH + OH \rightleftarrows H_2O + O$	k_9, K_9

The system was assumed to react at constant temperature, 2000°, and constant density beginning with only H_2 and O_2 present. The reaction rates and equilibrium constants used and the initial conditions assumed are shown in Table 2.8. Both forward and backward reactions were considered so that there are 9 independent uncertainties.

The early and late-time concentrations are shown in Figures 2.3 and 2.4. In Figure 2.3 the concentrations of H_2 and O_2 which are essentially unchanged from the initial conditions have not been shown. At early times the only reactions which contribute are numbers 1, 2, and 8 since no atomic O or H or OH is initially present. As more O, H, and OH become available, reactions 5, 6, and 7 become dominant which results in the sharp decrease in oxygen and hydrogen molecules and the correspondingly sharp increase of other species at $t \sim 10^{-3}$ sec. Finally, the slower reactions equilibrate slowly until a relative steady state is reached at about $t = 10^{-3}$ sec. This steady state is not true equilibrium in the sense that reactions 2, 5, and 8 are still quite far from equilibrium, but further relaxation to equilibrium is extremely slow.

Table 2.8

PARAMETERS AND INITIAL CONDITIONS FOR CALCULATIONS OF THE H-O SYSTEM

Initial Conditions:

$[H_2] = 8.0 \times 10^{-9}$ moles/cc

$[O_2] = 4.0 \times 10^{-9}$ moles/cc

Nominal Values of the Rate Coefficients:

$k_1^o = 5.78 \times 10^{4}$ $(\text{moles/cc})^{-1}$ sec^{-1}
$k_2^o = 4.47 \times 10^{3}$ "
$k_3^o = 1.03 \times 10^{5}$ "
$k_4^o = 6.79 \times 10^{5}$ "
$k_5^o = 1.23 \times 10^{12}$ "

$k_6^o = 4.0 \times 10^{13}$ $(\text{moles/cc})^{-1}$ sec^{-1}
$k_7^o = 1.51 \times 10^{13}$ "
$k_8^o = 2.20 \times 10^{6}$ "
$k_9^o = 1.6 \times 10^{14}$ "

Equilibrium Constants:

$K_1 = 1.59 \times 10^{-11}$ moles/cc
$K_2 = 2.69 \times 10^{-12}$ "
$K_3 = 1.14 \times 10^{-11}$ "
$K_4 = 1.63 \times 10^{-12}$ "
$K_5 = 2.37 \times 10^{-1}$ -

$K_6 = 1.4$ -
$K_7 = 9.76$ -
$K_8 = 2.02$ -
$K_9 = 6.76$ -

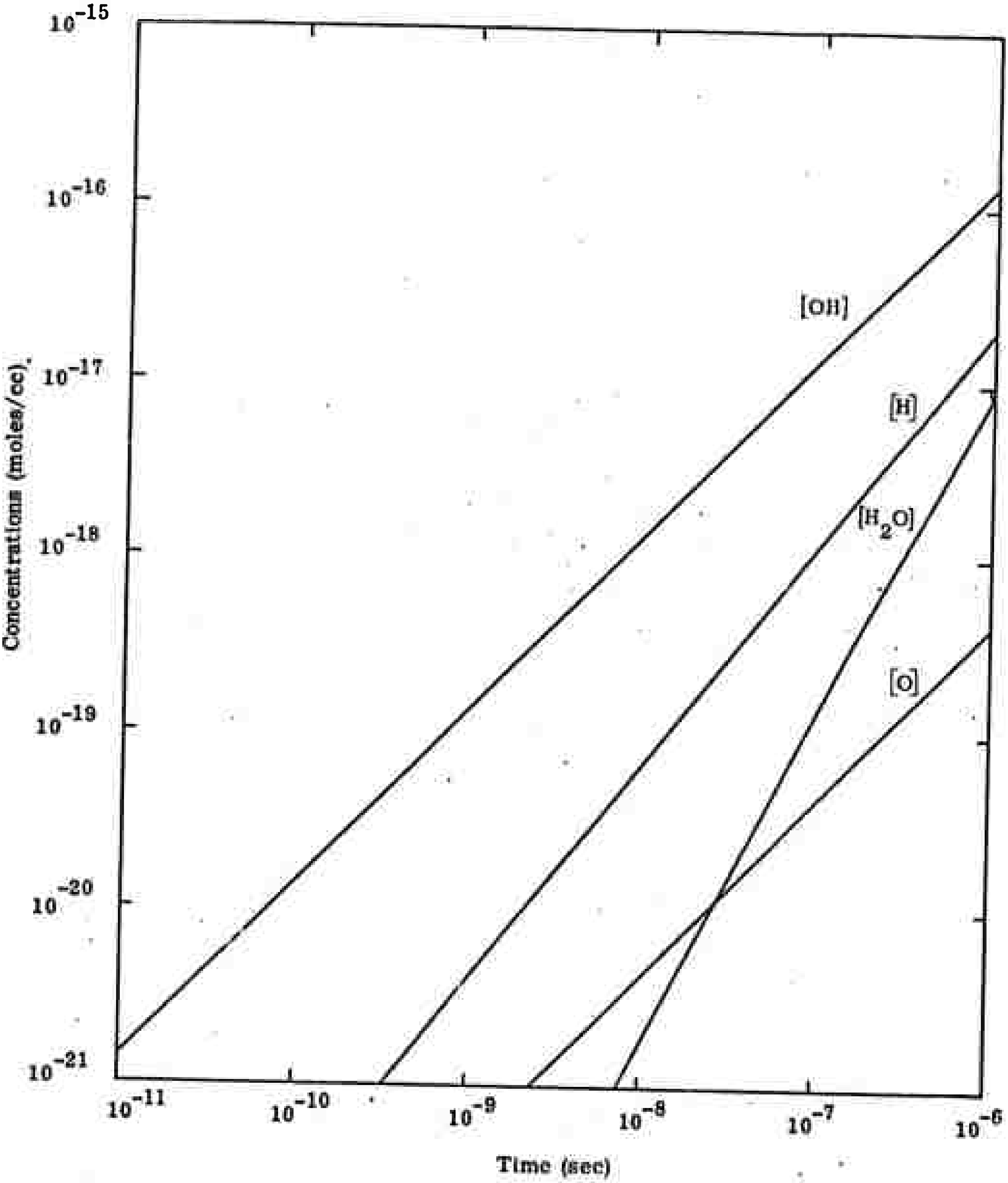

Figure 2.3 — Time evolution of the H-O system for the conditions in Table 2.8, $t = 10^{-11} - 10^{-6}$ sec.

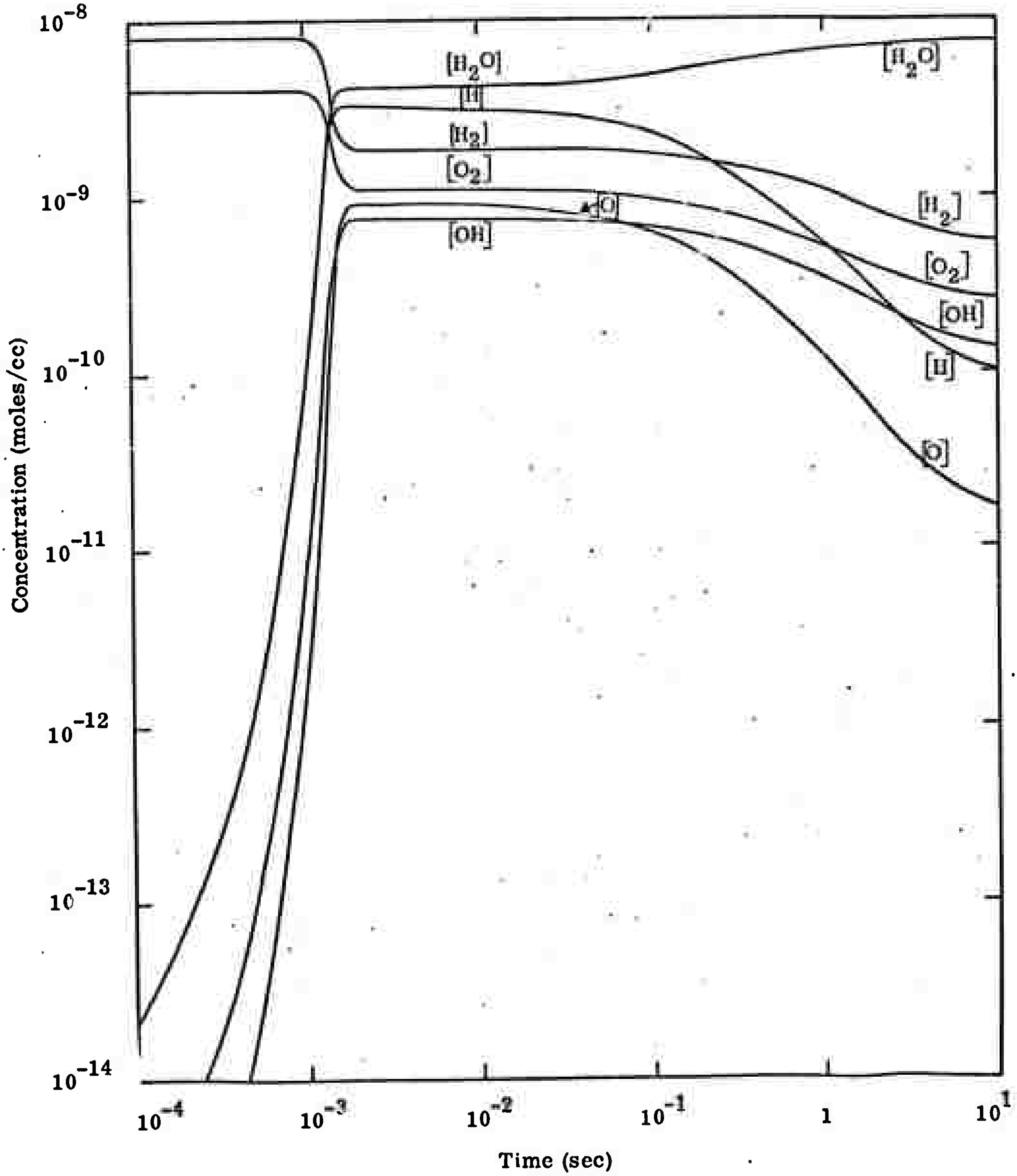

Figure 2.4 — Time evolution of the H-O system for the conditions in Table 2.8, $t = 10^{-4}$ - 10 seconds.

The rate constants shown in Table 2.8 are taken to be the "best guess" values and one order of magnitude uncertainty in each rate constant was assumed in order to demonstrate the technique. The frequencies for the analysis were taken to be the minimal set,

$$\bar{\omega} = (19,\ 59,\ 91,\ 113,\ 133,\ 143,\ 149,\ 157,\ 161)\quad .$$

630 evenly spaced points were taken on the s interval

$$0 < s \leq 2\pi$$

to evaluate the Fourier amplitudes. The analysis was run on the concentrations at one early time and one late time.

2.5.2.1 Interpretation of Results for the H-O System at 10^{-8} sec

The results for the sensitivity analysis for $t = 10^{-8}$ sec are shown in Table 2.9. At this very early time, the H_2 and O_2 concentrations have not varied from their initial values so that the sensitivity analysis showed their Fourier amplitudes to be very small, due only to roundoff in the analysis. The relative sensitivites of the other species, however, reflect the importance of the various reactions and the uncertainties in their rate constants. In the case of H, reaction 1 is the prime contributor and, therefore, its rate coefficient is crucial in determining the accuracy of [H]. k_8 and k_7 are also important since reactions 7 and 8 together produce H. The sensitivities of the two reactions are the same since, at early times these two reactions yield

$$[H] \propto k_7 k_8 \quad ,$$

and since the uncertainties $u_7^o = u_8^o$, the results are symmetric in k_7 and k_8. This is also the most efficient path to produce H_2O by at early times, and since there is a one to one correspondence between [H] and $[H_2O]$, the sensitivity of these concentrations to k_7 and k_8 are the same.

This system has not been run with a different frequency set to deduce the errors from interferences. It is estimated, however, for this set of results

Table 2.9

SENSITIVITY OF THE CONCENTRATIONS AT 10^{-8} SEC TO UNCERTAINTIES IN THE RATE COEFFICIENTS FOR THE H-O SYSTEM

Rate Coefficient	Sensitivity	Rate Coefficient	Sensitivity
$[H_2]$		$[O_2]$	
Insensitive to uncertainties in any rate constant.		Insensitive to uncertainties in any rate constant.	
$[H] \times 10^{11}$		$[O] \times 10^{20}$	
k_1	4.67	k_2	1.79
k_8	0.202	k_6	-0.016
k_7	0.202	k_1	0.0065
k_5	0.010	k_5	0.0065
k_6	0.0023	k_3	2.25×10^{-5}
k_2	0.00165	k_4	-1.95×10^{-5}
k_4	8.0×10^{-5}	k_9	7.87×10^{-6}
k_9	4.1×10^{-5}	k_8	1.20×10^{-6}
k_3	-3.0×10^{-5}	k_7	-8.46×10^{-7}
$[OH] \times 10^{18}$		$[H_2O] \times 10^{20}$	
k_8	5.9	k_8	2.03
k_7	-0.00203	k_7	2.03
k_9	1.76×10^{-3}	k_5	0.121
k_5	1.14×10^{-3}	k_6	0.0066
k_2	1.61×10^{-4}	k_4	8.35×10^{-4}
k_6	9.73×10^{-5}	k_1	-6.34×10^{-4}
k_1	7.08×10^{-5}	k_9	4.22×10^{-4}
k_4	-7.43×10^{-6}	k_3	-2.81×10^{-4}
k_3	3.13×10^{-6}	k_2	1.33×10^{-4}

that no credence should be given sensitivities smaller than 1 percent of the maximum for that species.

2.5.2.2 Interpretation of Results for the H-O System at 10^{-3} sec

At $t = 10^{-3}$ sec the system is about to make dramatic changes. Therefore, as the rate constants are shifted, one would expect the concentrations to change dramatically at $t = 10^{-3}$ sec. This is indeed the case, and one finds the various sensitivity results listed in Table 2.10. As predicted, reactions 5, 6, and 7 seem to be most important overall, with the early-time reactions 1, 2, and 8 of considerably less importance. It is clear that the controlling reactions affect all the species about equally which is to be expected, since all species appear in those reactions.

In running the H-O system to late times, difficulties were encountered with the equation integration package. The timesteps became excessively short, and often the input error criterion had to be modified in order to obtain a timely solution. The difficulties pointed up the need to investigate more closely methods for integrating the kinetic equations more economically.

2.6 COMPARISON OF THE FOURIER METHOD WITH OTHER METHODS FOR EVALUATING THE MULTIPLE INTEGRALS

It is possible to view the Fourier method as a means for approximately evaluating the multiple integral of an output function over u space. If incommensurate frequencies could be used, the evaluation would be exact. By using integer frequencies, the number of points required to determine the Fourier amplitude is finite, but an error is introduced because of the frequency interferences.

One way of obtaining the Fourier amplitudes without the troublesome interferences would be to evaluate the n-dimensional integral to which the amplitudes

Table 2.10

SENSITIVITY OF THE CONCENTRATIONS AT 10^{-3} SEC TO UNCERTAINTIES IN THE RATE COEFFICIENTS FOR THE H-O SYSTEM

Rate Coefficient	Sensitivity	Rate Coefficient	Sensitivity
$[H_2] \times 10^9$		$[H] \times 10^9$	
k_5	-3.71	k_5	1.92
k_7	-0.346	k_7	1.92
k_6	-0.313	k_6	0.122
k_8	-0.172	k_8	0.102
k_2	-0.108	k_2	0.061
k_4	-0.101	k_9	0.0466
k_9	-0.0905	k_4	0.0439
k_1	-0.0491	k_1	0.0176
k_3	0.0119	k_3	-0.00318
$[O_2] \times 10^9$		$[O] \times 10^{10}$	
k_5	-1.77	k_5	5.77
k_7	-0.153	k_7	0.420
k_6	-0.089	k_1	0.164
k_8	-0.070	k_6	0.162
k_2	-0.047	k_9	0.145
k_4	-0.047	k_2	0.116
k_9	-0.044	k_8	0.115
k_1	-0.031	k_4	0.10
k_3	0.0091	k_3	-0.061
$[OH] \times 10^{10}$		$[H_2O] \times 10^9$	
k_5	4.63	k_5	2.52
k_7	0.281	k_7	0.237
k_6	0.196	k_6	0.142
k_8	0.135	k_8	0.114
k_9	0.116	k_4	0.114
k_2	0.115	k_2	0.0718
k_4	0.0964	k_9	0.0614
k_1	0.0876	k_1	0.0358
k_3	-0.0359	k_3	-0.00851

correspond (see Equation 2.22) by an alternate method. One method which was tried was based on simple Monte Carlo integration. In this section we compare the Fourier method and the corresponding Monte Carlo calculations. Another equivalent form was investigated, namely integral I_3 in Appendix C which is an n-dimensional s integration equal to the u integral transformed by the relations

$$u_i = \sin \omega_i s \quad , \qquad i = 1, n \tag{2.39}$$

when the frequencies ω_i are those associated with the Fourier method. The function used in these comparisons was the "simulation function," Equation (3.3) with

$$C_1(\infty) = 0.1 \quad , \quad C_i(0) = 1$$

$$k_i = i \quad , \quad u_i^o = 0.5 \quad , \quad i = 1, 6$$

$$t = 1.5 \quad .$$

The results for the Fourier sine amplitudes of the input frequencies are denoted A_i , $i = 1, 6$. The frequencies were

$$(1, 21, 31, 37, 45, 49) \quad ,$$

201 points were used on the interval $(0, 2\pi)$ (no aliases interference of order less than 5). The amplitudes were run for 5 different permutations of frequencies, each of which defined a different path through the space. The results are shown in Table 2.11. The quantity in the column labeled "$\bar{A}$" is the average amplitude, and the "Maximum Error" is

$$\frac{\left|A - \bar{A}\right|_{\text{maximum}}}{\bar{A}}$$

Table 2.11

FOURIER AMPLITUDES FOR THE SIMULATION FUNCTION FOR FIVE CYCLICAL PERMUTATIONS OF THE FREQUENCY SET

Fourier Analysis

Permutation	1	2	3	4	5	6	Maximum Error
$A_1 \times 10^3$	-5.45	-5.51	-5.65	-5.75	5.92	5.65	4.8%
$A_2 \times 10^3$	2.67	2.80	2.72	2.70	2.93	2.76	6.2%
$A_3 \times 10^3$	-15.0	-14.7	-15.1	-15.3	-15.1	-15.04	2.3%
$A_4 \times 10^3$	7.02	7.0	7.12	6.94	7.11	7.04	1.4%
A_5	-3.36	-3.35	-3.35	-3.28	-3.46	-3.36	2.9%
A_6	-1.22	-1.26	-1.04	-1.20	-1.54	-1.25	23.2%

and serves as an estimate of the errors introduced by interferences.

The same one-dimensional integral was performed by Monte Carlo selecting the s points on the interval $(0, 2\pi)$ at random, and calculating an approximate integral

$$I_L = \frac{1}{2\pi N} \sum_{i=1}^{N} \sin \omega_L s_i \, f[k_1(s_i), \ldots, k_6(s_i)] \quad .$$

The results for the amplitudes for successive samples of 200 points is shown in Table 2.12. These results show that the number of points required by this Monte Carlo procedure to give statistical accuracy is much greater than the number required in the Fourier analysis. Stated another way, for 200 points, the degree of accuracy of the Fourier method far surpasses that of the Monte Carlo integration.

Another method was to select six values of u at random for each function evaluation, and approximate the integral by

$$I = \frac{1}{N\pi^n} \sum_{i=1}^{N} \frac{f_i \, u_i/u_i^o}{\sqrt{1-(u_i/u_i^o)^2}} \quad .$$

The results are shown in Table 2.13 for two successive sets of 200 points. While the error is much less in this case than in performing the one-dimensional Monte Carlo integral, the expected errors in a particular 200 point sample still greatly exceeds the errors in the Fourier sampling.

Monte Carlo was also used to evaluate the six-dimensional integral (I_3 of Appendix C) in s space choosing six independent values of s to insert separately into the integral. The results were comparable to those in Table 2.13 and will not be given.

Table 2.12

FOURIER AMPLITUDES FOR THE SIMULATION FUNCTION FOR FIVE SETS OF 200 POINTS

Monte Carlo

Permutation	1	2	3	4	5	$\bar{A}$	Maximum Error
$A_1 \times 10^3$	-5.0	-12.9	-9.62	-4.45	-2.55	-6.91	115%
$A_2 \times 10^3$	1.1	-8.9	-1.61	-5.09	-6.39	-9.45	900%
$A_3 \times 10^3$	-12.3	-22.4	-19.2	-9.7	-8.0	-14.3	56%
$A_4 \times 10^3$	9.3	9.5	4.10	2.73	7.89	6.69	60%
$A_5 \times 10^3$	-7.9	2.2	3.05	1.94	-11.8	-3.04	300%
$A_6 \times 10^3$	-5.3	-2.42	-0.73	-3.55	3.14	-0.061	~10^2

Table 2.13

EVALUATION OF THE MULTIPLE INTEGRAL IN u SPACE IN EQUATION (2.22) FOR TWO SETS OF 200 POINTS

Permutation	1	2	$\bar{A}$	Error
$A_1 \times 10^3$	-7.9	-5.2	-6.6	21%
$A_2 \times 10^3$	1.8	-3.1	-0.65	5%
$A_3 \times 10^3$	-15.5	-21.8	-18.6	17%
$A_4 \times 10^3$	7.9	15.3	11.6	32%
$A_5 \times 10^3$	-9.9	-4.65	-7.3	36%
$A_6 \times 10^3$	-2.8	-4.53	-3.7	24%

3. OPTIMIZATION OF AN OUTPUT FUNCTION WITH RESPECT TO VARIATIONS OF THE RATE COEFFICIENTS

An alternate method for investigating the variation of the calculated concentrations with variations of the rate constants was investigated in which the concentrations were optimized over the multi-dimensional domain of rate constants bounded by the maximum and minimum estimated uncertainties.

Several methods for optimizing functions of many variables have been well automated and are operational on the S^3 computer. A code CUK was written which solves the problem by the method of steepest ascents. This method proceeds by choosing the direction of the maximum gradient from a given starting point, and following that line to an extremum. The process is repeated by taking this as a new starting point, constructing a new line, following it to its extremum, and so forth until a relative extremum in the many dimensional space is found. A refinement to this technique using a sophisticated algorithm due to Davidon(1) and modified by Fletcher and Powell(2) and Stewart(3) is embodied in subroutines DMIN1 and DMIN2. In the Davidon algorithm, the search for a minimum proceeds along a line which does not exactly coincide with the gradient. At each step a new direction is chosen dependent not only on the gradient at the new starting point, but also on the previous history of the search. For some functions this procedure is much more efficient than one using the gradient directly. DMIN1 requires a subroutine which computes the gradient, which is essentially that described below, see Section 3.1. DMIN2 estimates the gradient by repeated evaluation of the function. Neither DMIN1 nor DMIN2 are capable of handling constraints, and an extension of Davidon's method to include constraints has been programmed into a subroutine called KEELE.

3.1 FORMULATION OF THE GRADIENTS FOR THE METHOD OF STEEPEST ASCENTS

Both DMIN1 and CUK require the gradient of the functions to be extremized. For the special class of output functions consisting of species concentrations as a function of time, the gradient may be integrated along with the rate equations to obtain gradients at any particular time.

A set of rate equations may be formally written

$$\frac{dC_i}{dt} = \sum_{j=1}^{n} \epsilon_i^j k_j \prod_{\ell \in L(j)} C_\ell^{m(j,\ell)} \quad , \tag{3.1}$$

where the index j label (separately) reactions in both forward and backward directions. L(j) is the set of indices corresponding to the reactant concentrations on the destruction side of the jth equation. ϵ_i^j is the stoichiometric coefficient of C_i if C_i is produced in the jth reaction, is equal to -1 if C_i is destroyed by the reaction, and is equal to 0 if C_i does not appear in the equation or appears with the same stoichiometric coefficient on both sides of the reaction. m(j, ℓ) is the stoichiometric coefficient of C_ℓ on the destruction side of the equation.

The partial derivatives of the ith concentration with respect to the pth rate coefficient, C_{ip}, are found by differentiating Equation (3.1) with respect to k_p

$$\begin{aligned} \frac{\partial C_{ip}}{\partial t} \equiv \frac{\partial}{\partial t}\frac{\partial C_i}{\partial k_p} &= \epsilon_i^p \prod_{\ell \in L(p)} (C_\ell)^{m(p,\ell)} \\ &+ \epsilon_i^{p*} \frac{k_{p*}}{k_p} \prod_{\ell \in L(p*)} (C_\ell)^{m(p*,\ell)} \\ &+ \sum_{j=1}^{n} \epsilon_i^j k_j \sum_{\ell'=1}^{n} m(p,\ell')(C_{\ell'})^{m(p,\ell')-1} C_{\ell',p} \prod_{\substack{\ell \in L(j) \\ \ell \neq \ell'}} C_\ell^{m(p,\ell)} \end{aligned} \tag{3.2}$$

p^* labels the reverse of reaction p, and the other symbols are defined after Equation (3.1). The second term on the right side of Equation (3.2) makes use of the assumption that k_{p^*}/k_p is a constant over the uncertainty space (i.e., there is no uncertainty in the equilibrium constant). This set of equations for $p = 1, n$ forms a linear set of equations in C_{ip} which can be integrated to obtain $C_{i,p}(t)$ by the same Gear algorithm used for integrating the basic rate equations. A version of the KEM code has been written to accomplish this.

3.2 TEST CALCULATIONS

Two types of test calculations were used to investigate the various methods of optimization. First, the properties of a "simulation function" were investigated to determine the consistency and relative economy of the various methods. Secondly, the CUK method was applied to the nitrogen-oxygen (N-O) chemical system.

A "simulation function" was suggested by Professor Shuler(4) which is not the solution to any known set of kinetic equations, but which possesses some of the same characteristics as kinetic solutions. The function is given by

$$C_1(t) = \left\{ C_1(0)\, C_1(\infty) \left[C_1(0) + \left\{ C_1(\infty) - C_1(0) \right\} e^{-k_1 t} \right]^{-1} + \frac{C_2^2(0)\, C_3^2(0)\, k_2 k_4 t^2\, e^{-k_3 t}}{C_3^3(0) + C_2^3(0)\, k_3 k_2 t^2} + \frac{C_4(0)\, C_5^2(0)\, k_4^3 t^3 \left(1 - e^{-k_3 t}\right) e^{-\left(\frac{k_5^2}{k_1 + k_2} t\right)}}{C_4(0)\, C_5(0) + C_3^2(0)\, k_4 k_5 t^2 + C_2(0)\, C_4(0)\, k_1 k_6^2 t^3} \right\} . \qquad (3.3)$$

$C_1(t)$ is a function of six rate constants as well as the time. The following substitution was made,

$$k_i = k_i^o e^{u_i} \tag{3.4}$$

so that the function is viewed as a function of u_i in the range

$$-u_i^o \leq u_i \leq u_i^o \quad , \quad i = 1, 6 \quad . \tag{3.5}$$

The time t was fixed at 1.5 so that only the functional dependence in u_i remains.

It is desirable to confine the domain of interest in u space to be contained within some n-dimensional box. Since some of the methods are designed for unconstrained systems, the above function was multiplied by an importance function to form the "associated simulation function"

$$P(\bar{u}) = e^{\sum_{i=1}^{n} -u_i^2/u_i^{o2}} \times C_1(t) \tag{3.6}$$

where $C_1(t)$ is given by Equation (3.3).

A comparison was made between the four methods: CUK, DMIN1, DMIN2, and KEELE. The output function is the associated simulation function described above, with the parameters shown in Table 3.1.

Table 3.1

PARAMETERS FOR THE OPTIMIZATION METHOD COMPARISON

Rate coefficient nominal values:	$k_i = 1, \ i = 1, 6$
Rate coefficient uncertainties:	$u_i^o = 1, \ i = 1, 6$
$t = 1.5$	
$C_i(0) = 1 \ , \ i = 1, 6$	
$C_1(\infty) = 0.1$	

The results using the four methods are shown in Table 3.2; all using comparable minimum step sizes of 10^{-5}. These results show that, for this function of six variables, the methods appear to be consistent.

Two starting points were tried, and for this output function, the same end point is reached. For complicated output functions, one would not expect the same end point for different starting points.

The cost of these calculations are all proportional to both number of function evaluations and the number of derivative evaluations. The relative economy of the CUK method over the more sophisticated methods led us to concentrate our further investigation on this method. For functions more complicated than the above, it is anticipated that the other methods might well be superior.

The CUK code was used on the associated simulation function for different parameters, and with different variations in the method. In the sets of results shown below, the parameters entering the associated simulation function were those given in Table 3.3.

Table 3.3

PARAMETERS ENTERING THE ASSOCIATED SIMULATION FUNCTION IN TEST PROBLEMS BELOW

Rate coefficients nominal values:	$k_1^o = 1$, $k_2^o = 2$, $k_3^o = 3$, $k_4^o = 4$, $k_5^o = 5$, $k_6^o = 6$
$C_i(0) = 1$, $i = 1, 6$,	
$C_1(\infty) = 0.1$	
$t = 1.5$	

Table 3.2

RESULTS OF COMPARISON OF OPTIMIZATION METHODS FOR THE ASSOCIATED SIMULATION FUNCTION

Part A: Minimum from Starting Point

$u_i^o = 0.1, \quad i = 1, 6$

	CUK	DMIN1	DMIN2	KEELE
Function Value	0.356846	0.356843	0.356755	0.356866
k_1	1.11918	1.11994	1.12342	1.11939
k_2	0.914977	0.909268	0.914298	0.915617
k_3	1.45013	1.44725	1.41251	1.45692
k_4	0.679556	0.669602	0.670227	0.677832
k_5	1.31851	1.32621	1.31683	1.32631
k_6	1.12414	1.12282	1.12951	1.12901
u_1	0.112598	0.113276	0.116388	0.112784
u_2	-0.088856	-0.095116	-0.089598	-0.088157
u_3	0.371653	0.369666	0.345370	0.376326
u_4	-0.386315	-0.401071	-0.400138	-0.388856
u_5	0.276503	0.282322	0.275225	0.282404
u_6	0.117014	0.115841	0.121783	0.121343
No. of Function Calls	46	115+	184	49
No. of Gradient Calls	10	25		24

Table 3.2 (Contd)

Part B: Minimum from Starting Point

$u_i^o = -0.1, \; i = 1, 6$

	CUK	DMIN1	CMIN2	KEELE
Function Value	0.356845	0.356839	0.356755	0.356841
k_1	1.12464	1.13471	1.12343	1.12512
k_2	0.916838	0.924054	0.914097	0.919816
k_3	1.44718	1.44315	1.41256	1.45030
k_4	0.670045	0.669190	0.670133	0.673464
k_5	1.29726	1.30969	1.31687	1.31326
k_6	1.12978	1.14590	1.12904	1.13609
u_1	0.117460	0.126376	0.116384	0.117894
u_2	-0.086825	-0.078985	-0.089819	-0.083581
u_3	0.369616	0.366831	0.345401	0.371773
u_4	0.400410	-0.401689	-0.400280	-0.395321
u_5	0.260252	0.269792	0.275258	0.272509
u_6	0.122021	0.136189	0.121367	0.127595
No. of Function Calls	40	604	284	51
No. of Gradient Calls	8	100		25

The results for both maximization and minimization of the associated simulation function are shown in Table 3.4. In Table 3.4, Part A, the maximum uncertainty in the rate coefficients is $u_i^o = 0.5$, in Part B the uncertainty is assumed to be $u_i^o = 1$.

3.2.1 Discussion of Table 3.4

Two methods were used to search for the maximum values of the function, constrained and unconstrained. In the constrained method, values of $\bar{u}$ were not allowed to be outside the box,

$$u_i = \pm u_i^o \quad . \tag{3.7}$$

When a gradient indicated that larger values of the function occurred outside this box, the direction of search was taken along the boundary. The results for the constrained and unconstrained maxima are therefore different for cases in which the maximum lies outside the box.

Each optimum of the function was evaluated for 2 or 3 starting points designated by the row labeled initial point. The columns labeled ±0.1 denote the initial point

$$u_i/u_i^o = \pm\, 0.1 \quad , \quad i = 1,\ 6 \quad . \tag{3.8}$$

The column denoted "corner" represents an initial point with coordinates given by the footnote asterisk,. The rows denoted k_i are the 6 values of the rate coefficients specifying the optimal values, and the u_i/u_i^o are then coordinates in u space normalized to a unit hypercube. In Part A, for example, the maximum unconstrained value of the associated simulation function is found at

$$u_5/u_5^o = -1.4 \quad ,$$

Table 3.4

RESULTS OF OPTIMIZATION OF THE ASSOCIATED SIMULATION FUNCTION (ASF)

Part A: Rate Constant Uncertainties

$u_i^o = 0.5, \quad i = 1, 6$

	MINIMUM			MAXIMUM				
				Constrained			Unconstrained	
Initial Point	0.1	-0.1	Corner*	0.1	-0.1	Corner**	0.1	Corner**
k_1	1.336502	1.336492	1.336565	0.942881	0.942877	0.942912	0.958178	0.986023
k_2	1.994806	1.994808	1.994806	2.038508	2.038510	2.038437	2.038124	2.54384
k_3	3.732751	3.732694	3.733028	1.819592	1.819592	1.819592	1.699020	2.84773
k_4	3.867460	3.867470	3.867411	4.777388	4.777428	4.777113	4.720191	5.715707
k_5	5.012121	5.012122	5.012120	4.998960	4.998960	4.999181	4.999231	2.47980
k_6	6.000996	6.000998	6.000997	5.999934	5.999934	5.999980	5.999951	4.99548
u_1/u_1^o	0.58	0.58	0.58	-0.12	-0.12	-0.12	-0.087	-0.028
u_2/u_2^o	-0.004	-0.007	-0.007	0.04	0.04	0.04	0.004	0.480
u_3/u_3^o	0.44	0.44	0.44	-1.0	-1.0	-1.0	-1.13	-0.1
u_4/u_4^o	-0.067	-0.069	-0.070	0.35	0.35	0.36	0.33	0.71
u_5/u_5^o	0.005	0.004	0.00[illegible]	-0.0005	-0.0004	-0.0005	-0.003	-1.4
u_6/u_6^o	0.001	-0.001	-0.001	-0.00005	0.00002	-0.00004	0.00002	-0.367
Optimal Value of the ASM	0.130960	0.130968	0.130968	0.173318	0.173318	0.173318	0.174365	0.161049
No. of Function Evaluations	102	75	56	62	57	65	61	58
No. of Derivative Evaluations	30	20	16	16	14	16	15	14

*Initial Point: $\bar{u}/u_i^o$ = (0.9, -0.8, 0.9, -0.9, 0.5, -0.5)

**Initial Point: $\bar{u}/u_i^o$ = (-0.5, 0.9, -0.7, 0.95, -0.95, -0.5)

Table 3.4 (Contd)

Part B: Rate Constant Uncertainties

$$u_i^o = 1, \; i = 1, 6$$

	MINIMUM		MAXIMUM			
			Unconstrained		Constrained	
Initial Point	0.1	Corner*	0.1	Corner**	0.1	Corner**
k_1	1.732245	1.732198	0.972464	0.891551	0.984629	0.885884
k_2	1.988241	1.988255	2.204691	3.334084	2.228403	2.814347
k_3	4.172935	4.172686	1.103638	2.881929	0.873297	2.93961
k_4	3.814059	3.814118	7.507727	10.87313	7.151887	14.42193
k_5	5.067699	5.067709	4.997028	1.839397	4.998524	1.49980
k_6	6.006362	6.006398	5.999815	3.641476	5.999911	3.740973
u_1	0.55	0.55	-0.028	-0.11	-0.015	-0.12
u_2	-0.005	-0.005	0.097	0.51	0.11	0.34
u_3	0.33	0.33	1.0	-0.04	-1.23	-0.02
u_4	-0.047	-0.047	0.63	1.0	0.58	1.28
u_5	0.014	0.014	-0.0006	-1.0	-0.0004	-1.2
u_6	0.002	0.002	-0.00002	-0.49	-0.0001	-0.47
Optimal Value of the ASM	0.126953	0.126953	0.352646	1.25303	0.376890	1.49207
No. of Function Evaluations $\Delta s=10^{-5}$ $\Delta s=10^{-2}$	56 32	69	51 36	45 26	73	39
No. of Derivative Evaluations $\Delta s=10^{-5}$ $\Delta s=10^{-2}$	15 9	19	12 10	10 7	30	8

*Initial Point: $\bar{u}$ = (0.95, -0.95, 0.95, -0.95, 0.7, -0.9)

**Initial Point: $\bar{u}$ (-0.5, 0.9, -0.7, 0.95, -0.95, -0.5) a point which is outside the uncertainty box, while in the constrained case, u_3 lies on the surface of the box, $u_3 = -u_3^o$.

In Part A, with the estimated uncertainty $u_i^o = 0.5$, $i = 1, 6$ the optimum function value is found to be independent of the initial point of the search for both the minimum and constrained maximum cases, but the unconstrained case finds different maxima. In Part B, even the maximum found in the constrained search is dependent on the initial point. This emphasizes the fact that such a search finds only a relative optimum which may be path dependent.

Finally, some words will be said about the numbers of function and derivative evaluations necessary to reach the optimum. These numbers depend strongly on the complexity of the output function. The method used by the CUK code is to select a direction based on a gradient calculation, and then search along that path with ever increasing distance until a functional optimum is found (or, if the search is constrained, until a boundary is reached). At this point, another gradient is calculated and the search proceeds along the new direction. The fact that the number of gradient calculations is small compared with the number of functional evaluations indicates that the gradient varies relatively slowly in the directions of search. Consistent with this observation are the last two rows in Table 3.4(B) which show that increasing the minimum step size from 10^{-5} to 10^{-2} (therefore increasing the average step size) reduces the number of function evaluations more than it reduces the number of gradient calculations.

An interesting feature of the associated simulation function is that the hyper-corner in which the maximum occurs is the reflection through the origin of the hyper-corner where the minimum is found (there are slight deviations from this principle in the case of u_6 in Part A for both the maximum and minimum. In each case, however, the values of u_6 are small so that difference of hyper-corner could be the effect of round-off error.)

3.3 RESULTS FOR THE N-O CHEMICAL SYSTEM

The N-O system investigated was the same as that for which test calculations were run using the Fourier method. The set of reactions chosen was:

$$O_2 + M \rightleftharpoons 2O + M \qquad k_1, K_1$$

$$N_2 + M \rightleftharpoons 2N + M \qquad k_2, K_2$$

$$NO + M \rightleftharpoons N + O + M \qquad k_3, K_3$$

$$N_2 + O \rightleftharpoons NO + N \qquad k_4, K_4$$

$$O_2 + N \rightleftharpoons NO + N \qquad k_5, K_5$$

The forward rate constants, k_i, and the equilibrium constants K_i were chosen as described in Table 2.4, with the exception that K_5 was set equal to 0.59 instead of 59.0. The uncertainty in each rate constant was assumed to be a factor $10^{\pm 2}$, that is, the rate coefficients were assumed to lie in the range

$$k_i = k_i^o e^{u_i} \tag{3.9}$$

$$-4.606 \leq u_i \leq 4.606 \quad .$$

The concentrations were initialized as shown in Table 3.5, and the system allowed to react isothermally at constant density until $t = 10^{-4}$ sec when the various species reach concentrations which were considered as output functions depending on the various rate coefficient uncertainties. The CUK code was used which is strictly a steepest ascents calculation. The hyperplanes defining the boundaries according to Equation (3.10) were taken to absolute constraints not to be violated.

The results of the optimization is summarized in Table 3.5 for the maximum of each concentration, and in Table 3.6 for the minimum of each concentration.

Table 3.5

RESULTS FOR THE MAXIMUM CONCENTRATIONS FOR THE N-O SYSTEM

	Initial Concentration (moles/cm^3)	Maximum Concentration (moles/cm^3) after 10^{-4} sec	Number of Function Evaluations	Number of Gradient Evaluations	Boundary Status
O_2	2.00×10^{-8}	1.98×10^{-8}	22	9	-----
O	0	4.00×10^{-8}	13	5	+---+
N_2	8.00×10^{-8}	8.00×10^{-8}	22	9	-----
N	0	8.58×10^{-8}	17	10	+-+++
NO	0	4.70×10^{-9}	38	16	M--M-

Table 3.6

RESULTS FOR THE MINIMUM CONCENTRATIONS FOR THE N-O SYSTEM

	Initial Concentration (moles/cm^3)	Minimum Concentration (moles/cm^3) after 10^{-4} sec	Number of Function Evaluations	Number of Gradient Evaluations	Boundary Status
O_2	2.00×10^{-8}	2.34×10^{-12}	16	9	++++-
O	0	9.12×10^{-11}	17	9	---+-
N_2	8.00×10^{-8}	3.69×10^{-8}	25	10	+-+++
N	0	1.77×10^{-15}	14	7	----+
NO	0	5.51×10^{-13}	18	10	+---+

In both tables, the columns need no further explanation except for the column designated "Boundary Status." The codes +, -, M have a meaning best described by example. The boundary status of N in Table 3.5 is +-+++. This means k_1, k_3, k_4 and k_5 equal to their upper experimental uncertainty limit and k_2 equals to its lower experimental uncertainty limit will produce the maximum concentration of N at 10^{-4} sec. If an M appears in the i th position from the left, the optimal value of the concentration occurred for a value of the i th rate coefficient between its upper and lower experimental uncertainties. Only in the case of the maximization of NO did the extremum lie at an interior point for a particular rate constant.

Another observation may be made that the hyper-corner in which the maximum is found is not the reflection of that for the minimum of the same species. In this way this chemical system is more complicated than the simulation function considered earlier. This may be understood in terms of the chemical kinetics by consideration of an example, the N concentration. In Table 3.6, the N concentration is shown to be minimized by maximizing k_5. Referring to the reaction set on page 59 this is reasonable since reaction 5 contributes strongly in the forward direction since, by minimizing k_1, there is an abundance of O_2 present. On the other hand, Table 3.5 also shows that the N concentrations will be maximized by maximizing k_5. In this case, k_1 is large so that there is an abundance of O atoms, and the reverse of reaction 5 dominates. Therefore, to increase k_5 increases the N concentration. It is questionable if results such as this could have been reached by chemical intuition alone, and we feel this exchange demonstrates a useful application of the method.

In addition to the information presented in Tables 3.5 and 3.6, one also has values of the gradients and output function at various points along a path from an initial point and the final optimum which can be useful and give a measure of the relative sensitivity of the output function to uncertainties in the various rate coefficients. The method has the characteristic that the sampling of points emphasizes either large values or small values of a particular output function which might be suitable for problems in which either values of a concentration above or below some threshold is of interest, for example, in the investigation of the onset of radar blackout in the atmosphere as a function of various rate coefficients.

The optimization methods have the disadvantage that a separate analysis must be made for each output function of interest, whereas, in the Fourier method, the sensitivity of all species in the system may be investigated by using the same sample of points.

The cost of the optimization procedure (for one concentration) is less than the Fourier method in the sense that fewer function evaluations are necessary. This effect is more than balanced, however, by the increased cost required to evaluate the gradients since, for n-independent reaction rates the cost of performing the time integration of the derivatives is approximately n^2 times greater than a calculation in which no gradients are computed. It may be that use of an optimization method such as DMIN2 or the SIMPLEX method$^{(5)}$ which replaces the gradient calculations by differences of previously calculated output functions may present a more economical alternative.

4. SUMMARY AND FUTURE EFFORTS

Two types of methods have been developed to investigate the sensitivity of the results of complex calculations to uncertainties in the parameters entering the calculations, the Fourier method, and the optimization methods. For a particular output function, the Fourier method provides a sensitivity number for each independent reaction rate coefficient whose magnitude characterizes the relative importance of the uncertainty in that coefficient in determining the uncertainty in the output function. This relative importance is an average importance over the many dimensional domain of the reaction rates consistent with the experimental uncertainty in each rate. The optimization methods investigate both the value of the output function and its gradient with respect to the rate coefficients. The latter is a measure of local sensitivity at a point. The uncertainty space is not sampled uniformly, but regions with either large or small values of the output function are treated preferentially. These two methods have application to distinctly different classes of problems.

For the real chemical systems considered so far, there are some features of the sensitivity results that can be predicted before the calculation. There are others that can not be easily predicted beforehand, but can be verified qualitatively by hindsight. The quantitative results (which of two important rate uncertainties is most important) are often extremely hard to predict on intuitive grounds alone, and demonstrate the utility of the methods.

At present we feel that both methods are useful in answering different questions about certain systems. Since the Fourier method is least understood, and appears to be most promising from the standpoint of economy, our immediate plans are to concentrate on this method. First priority is to apply the method to a wider class of non-equilibrium chemistry problems, in order to get a feel for the method. It will be advantageous for large systems (depending on more than, say, 20 independent reactions) to learn ways to split the system up into certain independent pieces for separate analysis. Another interesting question which will be addressed is to investigate alternate ways to calculate the multiple integral form of the Fourier coefficient using quadrature rules. This would eliminate the troublesome effects of interferences between frequencies.

There are improved optimization techniques which do not require the evaluation of the gradient, which may make these methods less expensive and, therefore, more useful. With these methods there is always the problem that an optimum is a local optimum and a global optimum requires many calculations beginning from different initial points. The selection of initial points is again a sampling problem, and it appears that considerable experience would be necessary to adequately investigate the uncertainty domain.

Another area for study is the selection of integration routines which will give results more economically. This is important since, for large systems, the calculation of the output function is the major expense. Perhaps accuracy could be sacrificed for speed in a sensitivity analysis.

Finally, the methods should be applied to a wide range of problems outside the area of non-equilibrium chemistry, for example, in the area of social systems modeling, or quality control modeling to determine their applicability to such systems.

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Appendix A

EQUIVALENCE OF RATIONAL AND INTEGER FREQUENCIES

Consider

$$I = \lim_{T\to\infty} \frac{1}{T} \int_0^T ds\, g\,(\sin\omega_1 s, \ldots, \sin\omega_j s, \ldots, \sin\omega_M s) \qquad (A.1)$$

where only a finite number, M, of rational frequencies are present. By rational frequencies we mean that they may be represented by

$$\omega_j = \frac{p_j}{q_j}$$

where p_j and q_j are relatively prime integers.

Let

$$\bar{q} = \prod_{j=1}^{M} q_j$$

and

$$\bar{q}\,\omega_j = \omega'_j ,$$

then $\bar{q}\,\omega_j = \omega'_j$ is an integer, and Equation (A.1) may be rewritten

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T ds\, g\,(\sin\omega'_1 s/\bar{q}, \ldots, \sin\omega'_M s/\bar{q}) \quad . \qquad (A.2)$$

But since g is a periodic function of $s' = s/\bar{q}$ with period 2π since all the

ω_j' are integers, this gives

$$I = \frac{1}{2\pi} \int_0^{2\pi} ds' \, g(\sin \omega_1' s', \ldots, \sin \omega_M' s') \quad . \tag{A.3}$$

The infinite integral in Equation (A.1) with rational frequencies is therefore equal to a finite integral with integer frequencies.

Appendix B

EXTRACTION OF FOURIER AMPLITUDES BY A FINITE SUM

The purpose of this Appendix is to show that one can evaluate the Fourier amplitudes of a periodic function f(s) by the following prescription

$$\left\{\begin{matrix} A_n \\ \\ B_n \end{matrix}\right\} = \frac{2}{N} \sum_{\ell=1}^{N} \left\{\begin{matrix} \sin (2\pi n \frac{\ell}{N}) \\ \\ \cos (2\pi n \frac{\ell}{N}) \end{matrix}\right\} f(2\pi \frac{\ell}{N}) + \text{alias amplitudes} \qquad (B.1)$$

where A_n is defined in Equation (2.7), and B_n is the corresponding cosine amplitude. n is an integer ≥ 0 and $f(2\pi) = f(0)$. We shall prove this relation for A_n, the sine amplitudes only, although the proof can be directly extended to the cosine amplitudes, B_n. Consider

$$A_n^* \equiv \frac{2}{N} \sum_{\ell=1}^{N} \sin 2\pi n \frac{\ell}{N} \, f(2\pi \frac{\ell}{N}) \qquad (B.2)$$

where

$$f(s) = B_o + \sum_{m=1}^{\infty} (A_m \sin ms + B_m \cos ms) \; .$$

Substituting f into A_n^* one must evaluate a sum of terms

$$A_{n,m}^* = \frac{2}{N} \sum_{\ell=1}^{N} \mathrm{Im}(e^{2\pi i n \ell/N}) \, A_m \sin(2\pi m \ell/N) \; , \qquad (B.3)$$

$$A^*_{n,m} = -\frac{1}{N} \operatorname{Re} \sum_{\ell=1}^{N} \left[e^{2\pi i(n+m)\ell/N} - e^{2\pi i(n-m)\ell/N} \right] A_m \qquad \text{(B.4)}$$

$$= -\frac{1}{N} \operatorname{Re} \left[\frac{e^{2\pi i(n+m)} - 1}{e^{2\pi i(n+m)/N} - 1} - \frac{e^{2\pi i(n-m)} - 1}{e^{2\pi i(n-m)/N} - 1} \right] A_m \qquad \text{(B.5)}$$

where we have used the formula

$$\sum_{\ell=1}^{N} r^{\ell} = (r^N - 1)/(r-1) \quad .$$

In the brackets each term vanishes unless the denominator vanishes since $e^{2\pi i p} = 1$ for p integer. Only special values of m relative to n will therefore contribute to A^*_n, and those are, for the first and second terms in the bracket, respectively,

$$m + n = qN \quad \text{condition 1} , \qquad \text{(B.6)}$$

and

$$|m - n| = qN \quad \text{condition 2} , \qquad \text{(B.7)}$$

where q is an integer ≥ 0. For $q = 0$, only $m = n$ contributes. For $q \geq 1$, let the special values of m satisfying conditions 1 and 2 be denoted $m^*_1(q, n)$ and $m^*_2(q, n)$, respectively. Then, for $N > n$, $m^*_1(q, n)$ will be distinct from $m^*_2(q, n)$ ($n = 0$ is an expection which is uninteresting), and every such m^*_1, and m^*_2 will contribute to A^*_n. Therefore

$$A^*_n = A_n + \sum_{q=1}^{\infty} \left[A_{m^*_1(q,n)} + A_{m^*_2(q,n)} \right] . \qquad \text{(B.8)}$$

The sum in the above expression may be viewed as an error term to the evaluation A_n. The amplitudes in the error term are called "alias amplitudes" since an amplitude for frequency $m^*(q, n)$ masquarades as one for frequency n. For $N \to \infty$, the error terms become small.

As discussed in Section 2.3.2 the input frequencies are chosen to be odd integers which have no interactions of order <5 which coincide with the input frequencies. Since the alias frequencies are equivalent to other frequencies, it is consistent to choose N sufficiently great that there are no aliases of interferences of order <5 which coincide with input frequencies either. Thus, N is chosen by trial and error so that condition 1 is satisfied,

$$\omega_i + \omega_m \neq qN \tag{B.9}$$

where ω_i is an input frequency and ω_m are all input frequencies and interferences of order less than or equal to 4. One can show that a sufficient condition to satisfy Equations (B.6) and (B.7) is

$$N > 4\,\omega_{max} \quad , \quad N_{even} \quad , \tag{B.10}$$

but by trial-and-error values of N slightly smaller than $4\,\omega_{max}$ may be found.

Appendix C

A THEOREM

In this Appendix we present a theorem which relates the Fourier amplitude of a function to an average of the output function over the n-dimensional space spanned by the rate coefficient uncertainties.

Theorem: Assume $f(u_1, u_2, \ldots, u_n)$ is a polynomial of order p-1 in the u's, over the domain

$$-u_1^o \le u_1 \le u_1^o$$

$$\vdots$$

$$-u_n^o \le u_n \le u_n^o \quad .$$

Assume also a set of integer input frequencies ω_i, $i = 1$, which are chosen so that no interferences of the order of less than p coincide with any input frequency. Then the Fourier amplitude corresponding to the Lth input frequency satisfies the following relation:

$$A_L \equiv \frac{1}{2\pi} \int_0^{2\pi} ds \sin \omega_L s \, f(u_1(s), u_2(s) \ldots u_n(s))$$

$$= \frac{1}{\pi^n} \int_{-u_1^o}^{u_1^o} du_1 \int_{-u_2^o}^{u_2^o} du_2 \ldots \int_{-u_n^o}^{u_n^o} du_n \frac{u_L \; f(u_1, \ldots u_n)}{u_L^o \prod_{i=1}^{n} u_i^o \sqrt{1 - (u_i/u_i^o)^2}} \tag{C.1}$$

where

$$u_i(s) = u_i^o \sin \omega_i s \quad .$$

Proof:

For convenience the two integrals in Equation (C.1) will be referred to as I_1 and I_2, respectively. The first step is to transform I_2 by the transformation

$$u_i = u_i^o \sin \omega_i s_i \qquad i = 1, n \tag{C.2}$$

then

$$I_2 = \frac{1}{(2\pi)^n} \int_0^{2\pi} ds_1 \int_0^{2\pi} ds_2, \ldots, \int_0^{2\pi} ds_n \sin \omega_L s_L f(u_1(s_1)\ldots u_n(s_n)) \tag{C.3}$$

$$\equiv I_3 \quad .$$

The next step is to show that $I_3 = I_1$.

Since f is a polynomial of degree p-1, we can expand it in a Maclaurin series

$$f(u_1, \ldots, u_n) = f_o + \sum_i f_i u_i + \sum_{i,j} f_{ij} u_i u_j + \ldots \tag{C.4}$$

where the last term contains a product of p-1 u's. Substituting Equation (C.2) for the u_i, $i = 1, n$, one obtains a series containing products of the form

$$\sin^{n_1}(\omega_1 s_1) \sin^{n_2}(\omega_2 s_2) \ldots \quad . \tag{C.5}$$

These terms may be expanded using the relation

$$\left(e^{i\omega_i s_i}\right)^{n_i} = e^{in_i \omega_i s_i} \quad .$$

Performing the s_i integrations one thus obtains

$$I_3 = u_L\left(\frac{f_L}{2} + \frac{1}{4}\sum_{i=1}^{n} f_{Lii}\, u_i^{o2} + \frac{1}{8}\sum_{i,j=1}^{n} f_{Liijj}\, u_i^{o2} u_j^{o2} + \ldots\right) \tag{C.6}$$

where all terms of f which are differentiated an odd number of time in u_L and an even number of times in all other u's contribute through derivatives of order $p-1$.

If one makes the substitution

$$u_i = u_i^o \sin \omega_i s \tag{C.7}$$

into the Equation (C.4) and substitutes that into I_1, one finds terms of the form

$$\sin^{n_1}(\omega_1 s) \sin(\omega_2^{n_2} s) \ \ldots \tag{C.8}$$

which is slightly different from Equation (C.5) in that the same s appears in each term in the product. The result is that when the expansion is made to reduce such a term to one linear in the sines or cosines, frequencies appear which are interferences of the input frequencies. In fact, since f is of order $p-1$ in the u's, interference frequencies which are of order $p-1$ will appear in the spectrum of f. But the frequency set was hypothesized to be free of $p-1$th order interferences coinciding with an input frequency such as ω_L. Therefore, only the terms in f which are of odd order in u_L and even order in all other u's will contribute. But that is the same set of terms as appears in I_3. Therefore,

$$I_1 = I_3 \ . \tag{C.9}$$

In the case that f is of higher order than p-1 in the u's, one can estimate the error between I_1 and I_3. ($I_2 = I_3$ independent of frequencies.) For definiteness, choose $p = 5$, which characterize the frequency sets used in the applications in Section 2, and assume f has a fifth order component

$$f_{jk\ell mq}\, u_j u_k u_\ell u_m u_q \tag{C.10}$$

with j, k, ℓ, m, q all different. Substituting according to Equation (C.2) into f in I_3 gives zero contribution to I_3. On the other hand, if one substitutes for this fifth order term into I_1 according to Equation (C.7), one can expand the product (C.10) to be

$$\frac{f_{jk\ell mq}}{16}\left[\begin{array}{l}\sin(\omega_1+\omega_2+\omega_3+\omega_4+\omega_5)s - \sin(\omega_1+\omega_2+\omega_3+\omega_4-\omega_5)s \\ +\sin(\omega_1+\omega_2+\omega_3-\omega_4-\omega_5)s - \sin(\omega_1+\omega_2+\omega_3-\omega_4+\omega_5)s \\ +\ldots\end{array}\right]. \tag{C.11}$$

If there exist frequencies $\omega_j, \omega_k, \ldots, \omega_q$ such that one of the 16 interference frequencies in Equation (C.11) coincides with ω_L, the contribution from the fifth order term will contribute to I_1. Since the order of this contribution is

$$O\left(f^{(p)}/2^{(p-1)}\right),$$

we can write for a general function f,

$$I_1 = I_2 + O\left(f^{(p)}/2^{(p-1)}\right). \tag{C.12}$$